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Widespread functional anoxia in the oxygen minimum zone of the Eastern South Pacific

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ABSTRACT

Oxygen minimum zones (OMZs) as found in the Eastern Pacific and Indian Ocean are biogeochemical hot spots with a disproportionately large role in the marine nitrogen cycle, and they are important components of the highly productive ecosystems in which they occur. Although the oxygen-depleted waters have been known for a century, oxygen levels inside them are not well constrained and the regulation of their anaerobic processes by oxygen is poorly understood. We deployed highly sensitive STOX oxygen sensors with a detection limit of 10 nmol kg^{-1} in combination with conventional hydrographic oxygen sensors along a cruise track transecting the Eastern South Pacific OMZ from South to North along the coast of Chile and Peru. Oxygen was below the detection limit throughout the $\sim 200 \text{ m}$ thick OMZ core in most casts with STOX sensors. The only exception was an offshore location off Peru where oxygen was $10\text{--}50 \text{ nmol kg}^{-1}$ in the core, likely as the result of a transient intrusion. Oxygen was also not detected in the OMZ core in further casts with conventional sensors, which had a detection limit of 90 nmol kg^{-1} after STOX-based zero calibration. Our measurements tighten the constraints on typical oxygen concentrations in the inner part of the OMZ by at least an order of magnitude relative to previous reports. Nitrite only accumulated when oxygen was depleted below 50 nmol kg^{-1} , which indicates that nitrogen cycling is much more sensitive to oxygen than previously estimated. We argue that extreme oxygen depletion to low nanomolar or even picomolar concentrations is a normal condition in the South Pacific OMZ, and suggest that the OMZ core is in fact functionally anoxic over wide regions for extended periods. Our results further indicate that oxygen dynamics in the low nanomolar range play an important role in OMZ biogeochemistry.

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1. Introduction

Following the first report of a pelagic oxygen minimum with “practically no oxygen at all” in the Pacific Ocean off Panama (Schmidt, 1925), similar conditions have been found to persist in wider parts of the Eastern North and South Pacific, in the Arabian Sea, and, to a lesser extent, in the South Atlantic off Namibia (Helly and Levin, 2004; Karstensen et al., 2008; Paulmier and Ruiz-Pino, 2009). These conditions result from a combination of stratification, sluggish circulation, and high oxygen consumption associated with organic matter sinking from productive surface waters (Wyrtki, 1962; 1967). Although waters of extreme oxygen depletion make up less than 0.1% of the ocean volume (Codispoti et al., 2001), they are important components of the marine

system. Thus, they support 25–50% of the removal of oceanic fixed nitrogen (Codispoti, 2007; Gruber, 2008) through anaerobic microbial processes including denitrification and anammox (Goering and Cline, 1970; Dalsgaard et al., 2003; Thamdrup et al., 2006) and are associated with a similar fraction of the oceanic N_2O emission (Bange, 2008; Naqvi et al., 2010). Unique nitrate-dependent benthic microbial communities thrive where the oxygen-depleted waters impinge on the seafloor (Fossing et al., 1995; Høglund et al., 2008), which is also an important site of phosphorite formation (Froelich et al., 1988; Föllmi, 1996).

Ongoing and forecasted expansions of OMZs (Stramma et al., 2008; 2010; Keeling et al., 2010) and of marine “dead zones” in general (Diaz and Rosenberg, 2008; Rabalais et al., 2010) emphasize the need for a detailed understanding of the role of these environments in the oceans. Fundamental to such an analysis are accurate definitions of oxygen distributions and dynamics within the OMZ, and how these conditions affect aerobic and anaerobic processes. Poor analytical resolution of oxygen at low concentrations is a major obstacle for further progress in this field (Ward

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et al., 2007; Jensen et al., 2008; Revsbech et al., 2009). Until recently, even very careful oceanographic surveys have reported detection limits for oxygen of about $1 \mu\text{mol kg}^{-1}$ (0.02 mL L^{-1}) (Cline and Richards, 1972; Paulmier et al., 2006). This is at least one order of magnitude higher than the half-saturation coefficient of oxygen respiration and aerobic growth in some bacterial cultures (Lloyd, 2002; Stolper et al., 2010) and natural microbial communities (Clement et al., 2009; Revsbech et al., 2009), and hence too high to resolve the oxygen-dependence of this process. Likewise, substantial aerobic oxidation of nitrite, ammonium, and manganese takes place at oxygen levels below detection by conventional methods (Lipschultz et al., 1990; Lam et al., 2007; Clement et al., 2009).

The oxygen threshold for anaerobic microbial processes leading to N_2 production in the OMZ is also not well defined. Recent OMZ budgets and models operate with thresholds ranging from 0.7 to $20 \mu\text{mol kg}^{-1}$ (see Karstensen et al., 2008; Paulmier and Ruiz-Pino, 2009). A high threshold is supported by some studies with pure cultures of denitrifiers (e.g., Betlach and Tiedje, 1981; Bonin et al., 1989), while the relative distribution of nitrite and oxygen in OMZs has been taken as an indication that nitrate reduction there is restricted to oxygen levels below 1 – $4.5 \mu\text{mol kg}^{-1}$ (Cline and Richards, 1972; Morrison et al., 1999; Codispoti et al., 2001). Also the absence of fixed nitrogen removal in the Bay of Bengal OMZ despite oxygen depletion to $\sim 3 \mu\text{mol kg}^{-1}$, points to a high oxygen sensitivity of these processes (Naqvi et al., 2005), and so do the low half-saturation coefficients for aerobic respiration (refs. above), since a tight coupling is expected between the oxygen dependence of aerobic respiration and the onset of nitrate reduction (Devol, 1978). Better analytical sensitivity is thus required to resolve the transition between aerobic and anaerobic respiration in OMZs, and also to evaluate the potential for interactions of aerobes and anaerobes at nanomolar oxygen levels (Lipschultz et al., 1990; Lam et al., 2007). Such improvements might further help to resolve specific issues such as the surprising differences in the importance of denitrification and anammox in between different OMZs (Ward et al., 2009) and the diverging conclusions concerning the relative importance of these processes in the Arabian Sea (Ward et al., 2009; Jensen et al., 2011).

With a detection limit of $0.01 \mu\text{mol kg}^{-1}$ or better, the newly developed STOX oxygen sensor greatly improves the prospects of

resolving oxygen dynamics in OMZs and determining the oxygen dependence of microbial processes (Revsbech et al., 2009; 2011). In the first in situ deployment of the STOX sensor at a station off Peru, oxygen was not detectable ($< 2 \text{ nmol kg}^{-1}$) through the OMZ core, i.e., the system was essentially anoxic (Revsbech et al., 2009). Oxygen was also not detected in the OMZ core in two further deployments off Chile (Canfield et al., 2010) nor in one in the Arabian Sea (Jensen et al., 2011), with detection limits of 13 and 90 nmol kg^{-1} , respectively, suggesting that extreme oxygen depletion may be a common phenomenon.

In order to provide a more detailed description of oxygen levels and their distribution in an OMZ core, and thereby more accurately define the conditions for biogeochemical processes, we used a combination of measurements with STOX and conventional sensors to determine oxygen along a transect through the OMZ of Eastern South Pacific from 5° to 28°S . We further used the relative distribution of oxygen and nitrite, the key intermediate in the reductive pathways of the nitrogen cycle, to analyze how oxygen affected the net balance of oxidative and reductive nitrogen metabolisms.

2. Materials and methods

All measurements were made between 12 and 24 February 2007 during legs 13 and 14 of the Danish Galathea-3 Expedition (Fig. 1; Table 1). STOX (Switchable Trace amount OXygen; Revsbech et al., 2009) and two Seabird SBE43 oxygen sensors were mounted on a Seabird SBE911 CTD (Conductivity–Temperature–Depth probe) associated with a SBE32 rosette carrying ten 30-L Niskin bottles. Sensor configuration, mounting, data acquisition, and calibration were previously described (Revsbech et al., 2009), except the zero correction of the SBE43 oxygen data, which is described below. Data for this study was acquired at a rate of 24 s^{-1} during the upward part of the hydrographic casts. STOX sensors contain a front guard cathode, which is intermittently polarized at -0.8 V to keep oxygen from reaching the measuring cathode and permit zero calibration in situ. The sensors were operated in a 60 s cycle with the front guard cathode polarized for 20 s (zeroing) and depolarized for 40 s (measurement), and data collected from 6 to 1 s before each switch in polarization was used for oxygen determination (Revsbech et al., 2009). The

Fig. 1. Locations sampled along the coast of Peru and Chile. Oxygen was determined with highly sensitive STOX sensors at locations within the black rectangles. The map to the left shows the densely sampled area off Pisco with cast numbers. Locations along the black line were included in the transect in Fig. 2.

Table 1
Positions and depths of hydrographic casts, availability of STOX oxygen data, and usage of SBE43 oxygen data.

Cast ID	Southern latitude	Western longitude	Bottom depth, (m)	Cast depth, (m)	STOX data	SBE43 data ^a
13.1	29°17.13	071°52.98	3646	500	–	> 25 $\mu\text{mol kg}^{-1}$
13.2	26°18.26	071°15.74	4740	501	–	Corrected
14.1	23°37.36	070°52.63	3022	501	–	Corrected
14.2	20°03.46	070°45.27	1480	200	+ ^b	Not shown
14.6	20°03.47	070°45.37	1498	500	–	Corrected
14.14	18°30.04	071°00.13	1203	499	–	Corrected
14.17	17°05.14	072°25.14	1222	499	–	Corrected
14.21	15°30.03	075°44.74	3135	500	–	Corrected
14.25	14°22.92	076°23.85	313	301	+	Not shown
14.31	14°14.19	076°36.45	998	501	+ ^c	Zero calib.
14.32	14°14.22	076°36.12	980	500	+	Not shown
14.38	14°14.18	076°36.36	1020	1014	+	Not shown
14.47	14°23.52	076°25.58	393	382	+	Zero calib.
14.56	14°23.57	076°25.50	388	152	+	Not shown
14.73	13°52.23	076°47.99	736	400	+	Zero calib.
14.74	14°16.62	076°47.43	2370	500	+	Zero calib.
14.77	14°16.59	076°47.60	2426	500	+	Zero calib.
14.85	14°09.79	077°25.72	5153	500	+	Not shown
14.86	14°09.70	077°25.79	5155	500	+	Not shown
14.96	13°49.08	076°45.89	617	508	–	Corrected
14.100	12°26.62	077°36.94	583	502	–	Corrected
14.121	09°29.84	079°39.95	843	500	–	Corrected
14.122	07°30.01	080°60.00	2339	502	–	Corrected
14.129	05°15.27	081°34.68	3016	416	–	> 3 $\mu\text{mol kg}^{-1}$

^a “Corrected”: data corrected according to Eq. S1 and included in Fig. 1. “Not shown”: data from stations outside the transect in Fig. 1. “Zero calib.”: cast with simultaneous STOX and SBE43 oxygen determination used for zero calibration (Fig. S1). At stations 13.1 and 14.129 oxygen was not fully depleted and hence no zero correction was applied.

^b Detection limit approx. 30 nmol kg^{-1} due to slow response time of STOX sensor.

^c Results from 201 to 120 m depth were previously published by Revsbech et al. (2009).

upward casts were made at approx. 0.4 m s^{-1} interrupted by stops of 3 min or longer at specific depths. Thus, during stops, oxygen concentrations were determined from the average of typically three cycles of the STOX sensor, while concentrations determined during profiling represent data collected over 2 m with zero calibration performed 16 m below and 8 m above. STOX sensors were deployed successfully in 11 hydrographical casts off Peru around 14°S and once at 20°S off Chile. The detection limit for the Peru deployments was 10 nmol kg^{-1} estimated as 3 standard deviations of single-cycle oxygen determinations during stops within the OMZ core. In the deployment off Chile, the detection limit was 30 nmol kg^{-1} due to a slow response time of the measuring circuit, which prevented the signal from stabilizing during the cycles of front-guard polarization.

Data from the SBE43 oxygen sensors was initially converted to oxygen concentrations by standard procedures using the coefficients for calibration and temperature and pressure correction determined by the manufacturer. The validity of the calibration in the normal concentration range was checked against Winkler titrations during the cruise and verified in the laboratory after the expedition, showing negligible drift. The data was filtered electronically with a 0.15 s low-pass filter and binned in 1 s time intervals. Comparison of the results from SBE43 sensors to those from the STOX sensor demonstrated characteristic reproducible responses of the SBE43 sensors in waters where oxygen was not detected by the STOX sensor, which allowed a recalibration of the SBE43 data, as described in Section 3.2.

Water for nitrite and nitrate analysis was collected in the Niskin bottles during the stops in the upward casts. The bottles were closed at the end of each stop. Nitrite was analyzed

spectrophotometrically (detection limit $0.1 \mu\text{mol L}^{-1}$, typical S.D. $0.05 \mu\text{mol L}^{-1}$; Grasshoff, 1983) and nitrate + nitrite was analyzed by NO chemiluminescence after reduction with V^{3+} (relative S.D. 5%; Braman and Hendrix, 1989). Isopleths were plotted using Ocean Data View v. 4.3.6 (Schlitzer, 2010).

3. Results and discussion

3.1. General oceanographic conditions

The measurements were made 2–3 months after a weak El Niño event that peaked in November 2006, and the oceanographic conditions in the ETSP had just returned to the normal range as indicated by the Oceanic Niño Index (NWS Climate Prediction Center). Sea surface temperatures along the cruise track were at or slightly ($< 1^\circ\text{C}$) above the normal for February (NASA Earth Observations), and the distribution and concentrations of chlorophyll as estimated from satellite closely resembled the monthly climatology for the past decade (OceanColor Web).

The depthwise and meridional distributions of salinity and temperature (Fig. 2) were also similar to previous reports (Silva et al., 2009 and refs. therein). Thus, as described by Silva et al. (2009), Equatorial Subsurface Water (ESSW) dominated the upper 500 m, with its salinity core (34.9) shoaling from $> 200 \text{ m}$ at 5°S to $\sim 100 \text{ m}$ at 15–20°S, south of which it was eroded, such that at 28°S a maximum salinity of 34.6 was reached at 200 m. Below the ESSW core, salinity gradually decreased towards a minimum of 34.55 reached at 700–900 m depth (not shown), which represents the much eroded northern extension of the Antarctic Intermediate Water (AAIW). Along the northern and central Peruvian coast the ESSW was directly overlain by more saline Subtropical Water (STW; core characteristics: $\geq 20^\circ\text{C}$, $S=35.2$) whereas south of 15°S a shallow salinity minimum of ≤ 34.8 was present between the ESSW and the STW as previously described (Silva et al., 2009 and refs. therein). This minimum, which was as shallow as 30 m at 17–20°S, is attributed to a tongue of Subantarctic Water (SAAW) often referred to as Eastern South Pacific Intermediate Water (ESPIW; Schneider et al., 2003; Silva et al., 2009).

3.2. Oxygen in the OMZ

Oxygen was consistently below the detection limit of the STOX sensors throughout the approximately 200 m-thick OMZ core in 10 out of 12 profiles, including nine recorded 20–55 km off the Peruvian coast around 14°S as well as the one from 20°S off Chile (Fig. 3(a)). Complete oxygen depletion coincided with densities (σ_θ) of $26.1\text{--}26.7 \text{ kg m}^{-3}$ ($T=10\text{--}14^\circ\text{C}$; $S=34.7\text{--}34.9$), respectively. By contrast, $10\text{--}50 \text{ nmol kg}^{-1}$ oxygen was detected through most of the OMZ core in two casts at a station 120 km off the coast of Peru (Fig. 3(b); casts 14.85 and 14.86). There was a good agreement between oxygen determinations from coinciding depths from these two casts, which were separated by an interval of 2 h. Thus, oxygen in both profiles increased from $\leq 10 \text{ nmol kg}^{-1}$ in single determinations at $\sim 300 \text{ m}$ to $> 40 \text{ nmol kg}^{-1}$ at 250 m, decreasing again to 10 nmol kg^{-1} at 180 m. Both profiles also showed a peak with up to 400 nmol kg^{-1} between 50 and 80 m depth. The salinity-temperature relationship showed disturbances in the stratification at the depths where oxygen was detected (Fig. 4). This was seen as two intrusions of less saline water at $11.0\text{--}12.3^\circ\text{C}$ and above 12.7°C , respectively, relative to the mixing line between Equatorial Subsurface Water and Antarctic Intermediate Water, while the S-T relationship followed this line more closely at most other stations. The deeper intrusion extended to densities of $26.60\text{--}26.62 \text{ kg m}^{-3}$ corresponding to depths of 275–280 m, while no disturbance was observed at 300 m, consistent with the lack of detectable oxygen at

Fig. 2. Distribution of temperature ($^{\circ}\text{C}$), salinity (psu), and oxygen ($\mu\text{mol kg}^{-1}$) based on corrected data from the SBE43 sensor, along the west coast of South America in February 2007 (transect in Fig. 1). Vertical lines indicate sampling locations. For oxygen, isopleths are plotted in black for the detection limit of 90 nmol kg^{-1} and for thresholds previously used to define oxygen minimum zones. Isopycnals for the densities (σ_{θ}) 26.1 and 26.8 kg m^{-3} are plotted in white.

this depth (Figs. 3b and 4). The oxygen minimum at 180 m coincided with the water layer that separated the two intrusions, which further substantiated the link between the presence of oxygen and the intrusions. While a salinity minimum originating from SAAW/ESPIW is occasionally present above 12°C , the deeper intrusion to 11°C seems atypical in this region (e.g., Huyer et al., 1978; Copin-Montegut and Raimbault, 1994). Thus, the deep penetration of nanomolar oxygen levels was likely a transient phenomenon, although the possibility that it represented a more general inshore-offshore trend in oxygen levels cannot be completely ruled out without measurements further off shore.

At the stations off Peru, the upper boundary of complete oxygen depletion was located at 100–120 m depth (Fig. 3(a)). In most of the casts, oxygen remained below $3 \mu\text{mol kg}^{-1}$ upwards from this boundary to 30–60 m depth, with higher concentrations in the deeper part of the low-oxygen zone and a secondary minimum near its upper boundary. Concentrations in this shallow minimum were generally below $1 \mu\text{mol kg}^{-1}$, and in two casts

(14.31 and 14.73°S) complete oxygen depletion was detected at 60 and 30 m depth, respectively, corresponding to densities of 25.91 – 25.94 kg m^{-3} . Due to the discrete mode of STOX sensor measurements, oxygen-depleted layers of few meters thickness would only be detected with certainty if they coincided with stops in the CTD cast. Thus, similar oxygen depleted layers could easily have been missed in other casts.

Simultaneous deployment of STOX and conventional SBE43 oxygen sensors allowed accurate zero-point calibration of the conventional sensors and thereby the extension of our analysis to the entire cruise track, as well as an evaluation of the continuity of oxygen levels at depths between the STOX measurements. The SBE43 sensors exhibited a characteristic slow asymptotic decrease in signal in the core of the OMZ where oxygen was not detected by the STOX sensor (Fig. 5(a), (b) and Fig. 6). The decrease in signal was independent of whether the instrument was profiling or stopped at a given depth, and the response was highly reproducible for each sensor for casts to 400–500 m depth.

Fig. 3. Depth distributions of oxygen through the core of the oxygen minimum zone off Peru as determined in situ with STOX oxygen sensors. Filled symbols represent measurements at fixed depth with standard deviation of replicates ($n=3-4$) while open symbols represent measurements recorded during profiling. (a) Results from eight casts no. 14.10–14.77. (b) Results from two casts (14.85, triangles, 14.86, circles) from the location furthest off shore (Fig. 1), with corrected oxygen concentrations from the SBE43 sensor from cast 14.85 shown as a grey line with measurements below the detection limit of $0.09 \mu\text{mol kg}^{-1}$ omitted for clarity. The large error bars associated with stationary measurements above 125 m depth reflect temporal fluctuations in the oxygen concentration during the measurement in the steep oxycline.

We attribute the time-dependent signal to oxygen released from the plastics of the SBE43 sensors and the flow-through system in which they are mounted. The drift was strongest during the downward cast (see Revsbech et al., 2011). For further analysis, we therefore used data from the upward casts, where the drift typically amounted to $0.5 \mu\text{mol kg}^{-1}$ during the passage through the OMZ core. The readings from the two SBE43 sensors agreed within $0.1 \mu\text{mol kg}^{-1}$ in the oxygen-depleted core (data not shown), and data from one sensor was used for further calculations. An ad hoc zero correction of the SBE43 oxygen data was derived by fitting the empirical time-dependent asymptotic function $C(t) = a e^{-b(t-t_0)} + c$ to the uncorrected SBE43 oxygen reading during the passage of the oxygen depleted zone, with t_0 representing the time of entrance to the oxygen-depleted core (Fig. 5(c)). When the CTD first entered the oxygen-depleted core from below the SBE43 sensor had an oxygen reading of $1.7 \mu\text{mol kg}^{-1}$ and t_0 was thus defined as the time when the SBE43 reading decreased below this value. In cast 14.47, for example, the deepest depth where oxygen was undetectable with the STOX sensor was 296 m and the SBE43 reading here was $1.7 \mu\text{mol L}^{-1}$ (Fig. 5(a)). The reading decreased below $1.7 \mu\text{mol L}^{-1}$ at an acquisition time of 1616 s (Fig. 5(b)), which was consequently defined as t_0 (Fig. 5(c)). Data from five casts

Fig. 4. Salinity-temperature diagrams for casts 14.85 and 14.86 at a position 120 km off shore, compared to typical values from other stations, exemplified by casts 14.17 and 14.62 with and without the presence of Eastern South Pacific Intermediate Water (ESPIW), respectively. The typical linear relationship between temperature and salinity at 7–13 °C in casts 14.17 and 14.62 represents the transition between Antarctic Intermediate Water (AAIW; $T=5^\circ\text{C}$) and Equatorial Subsurface Water (ESSW; $T=13^\circ\text{C}$). The grey lines indicate specific densities (σ_θ) of 26.1 and 26.7 kg m^{-3} between which the OMZ core is located. The deviation of the T–S relationship from the linear relationship in casts 14.85 and 14.86 indicates intrusions, which reached a depth of 280 m indicated by the arrow, and coincided with the detection of $10-50 \text{ nmol kg}^{-1}$ of oxygen (Fig. 3(b)).

were used for a non-linear least-squares fit of the function, yielding the parameters $a=0.598 \mu\text{mol kg}^{-1}$, $b=0.00148 \text{ s}^{-1}$, $c=1.08 \mu\text{mol kg}^{-1}$. The SBE43 oxygen data were corrected by subtraction of the parameterized function from the uncorrected reading (Fig. 6):

$$\text{O}_2 \text{ SBE43 corrected} = \text{O}_2 \text{ SBE43 uncorrected} - ae^{-b(t-t_0)} - c \quad (1)$$

The detection limit of $\text{O}_2 \text{ SBE43 corrected}$ was $0.09 \mu\text{mol kg}^{-1}$, estimated as 3 times the standard deviation of $0.029 \mu\text{mol kg}^{-1}$ of the values obtained in the OMZ core where oxygen was not detectable with STOX sensors (Table 2).

The corrected SBE43 data revealed a contiguous, 200–300-m deep zone with no detectable oxygen along 1180 km of the transect between 12.5° and 20°S (Fig. 2(c)). Complete oxygen depletion was also found north and south of this section, from 7.5° to 26.5°S , covering 2500 km of the transect, but here it was restricted to thinner layers bordered by intrusions containing 0.2 to $3.2 \mu\text{mol kg}^{-1}$ oxygen. There was a good agreement between corrected SBE43 data and STOX data in the low-oxygen layer overlying the OMZ core (example from cast 14.85 in Fig. 3(b)), which confirmed the ability of the SBE43 sensors to resolve submicromolar concentrations after proper zero calibration, and further revealed the complicated structure of oxygen distributions in this layer. The oxygen-depleted water mass grew in thickness from ~ 200 m at latitudes north of 15°S to 300 m at 20°S , corresponding to densities (σ_θ) of $26.15-26.8 \text{ kg m}^{-3}$ and $26.10-26.7$, respectively (Fig. 2(c)). It corresponded closely to the core of the ESSW, being restricted downwards, towards the AAIW, and to the South to salinities above 34.75, while the upper limit was at 34.95 towards the STW and at 34.80 in the presence of the ESPIW (Figs. 2(b) and (c), 4).

Both the horizontal and vertical extent of oxygen depletion agree well with previous descriptions of the distribution of waters with oxygen at or below the detection limit in the inner part of the South Pacific OMZ (e.g., Wooster and Gilmartin, 1961; Zuta and Guillen, 1970; Codispoti and Packard, 1980; Silva et al., 2009). However, our measurements tighten the constraints on oxygen in

Fig. 5. Zero calibration of SBE43 oxygen data. SBE43 oxygen data from stations where the STOX oxygen sensor demonstrated complete oxygen depletion in the OMZ core. (a) Profiles of uncorrected oxygen readings from the SBE43 sensor (O_2 SBE43 uncorrected) from five casts through the OMZ core, as recorded during the upward cast. Thick vertical lines to the left indicate the depth intervals where oxygen was depleted below the detection limit of the STOX sensor. In casts 14.31 and 14.73, thin secondary oxygen depleted layers were detected above the OMZ core around 30 and 60 m depth as indicated by short horizontal lines. (b) Same data as in (a) plotted as function of deployment time. The horizontal black line indicates the threshold of $1.7 \mu\text{mol kg}^{-1}$ in O_2 SBE43 uncorrected, which corresponds to the onset of anoxia as demonstrated by STOX oxygen data. (c) Same data as in (b) plotted as function of time relative to the time when O_2 SBE43 uncorrected dropped below $1.7 \mu\text{mol kg}^{-1}$. The double line represents the least-sum-of-squares fit of the function $a e^{-b(t-t_0)} + c$ to the data (see text for details).

the core of the OMZ by two to three orders of magnitude relative to the previous reports that constrained oxygen to less than $1\text{--}5$ (~ 10) $\mu\text{mol kg}^{-1}$ depending on the analytical sensitivity. The geographic extent of oxygen depletion (Fig. 2(c)) and its tight association with the ESSW under normal hydrographical conditions, indicate that oxygen depletion to $< 0.09 \mu\text{mol kg}^{-1}$ is a normal phenomenon in the Eastern South Pacific OMZ. The ESSW is transported southward by the Peru–Chile Undercurrent at core velocities of $5\text{--}10 \text{ cm s}^{-1}$ (Wooster and Gilmartin, 1961; Fonseca, 1989; Czeschel et al., 2011) corresponding to 4–9 months for the 1180 km distance with full oxygen depletion (see Codispoti and Christensen, 1985, for a similar estimate of residence time). Considering a residence time of the ESSW

Fig. 6. Examples of zero correction of oxygen data from the SBE43 sensor from casts where STOX sensor data were not available. (a) Profiles of uncorrected readings through the OMZ core from upward casts. (b) Same data plotted as a function of time relative to the time when the O_2 SBE43 uncorrected dropped below $1.7 \mu\text{mol kg}^{-1}$. The double line represents the zero correction derived from simultaneous STOX and SBE43 oxygen determinations in other casts (Fig. 5).

of several months as well as the relatively weak seasonality in oxygen distributions in the ESP OMZ (Paulmier and Ruiz-Pino, 2009), our oxygen measurements may indeed represent typical conditions in the inner part of the Eastern South Pacific OMZ. For the southern part of the OMZ, this is supported by further oxygen determinations with STOX sensors at 20°S (close to our cast 14.6), which found oxygen to be undetectable in several casts in both August 2009 and January 2010 (Canfield et al., 2010; unpubl. results).

The stations with oxygen depletion were located 22–130 km from shore, and should thus be representative of the 175 km wide inner zone of the South Pacific OMZ that was previously estimated to house 76% of its denitrification (Codispoti and Packard, 1980). Under the conservative assumption that they are representative of a zone of at least 50 km width, we estimate a total volume of oxygen-depleted water ($< 0.09 \mu\text{mol kg}^{-1}$) of at least $2.4 \times 10^{13} \text{ m}^3$, based on the 480 km^2 cross section held within the $0.09 \mu\text{mol kg}^{-1}$ isopleth along the transect (Fig. 2(c)). The cross section was determined graphically by plotting the isopleth with distance rather than latitude on the x-axis. This volume is 24 times larger than the most recent estimate of suboxic ($< 4.5 \mu\text{mol kg}^{-1}$) water in the Eastern South Pacific (Karstensen et al., 2008). The volume corresponding to the 1180 km of the transect with massive oxygen depletion (average core thickness 250 m) was $1.5 \times 10^{13} \text{ m}^3$, which is still 15 times higher than the previous estimate. Thus, oxygen depletion was not only much more severe than previously known; extreme depletion also affected a far greater volume than previously documented. We attribute this difference primarily to the improved sensitivity of the oxygen analysis. Our strategy of sampling along the coast may also have contributed, since this region is poorly represented in some ocean databases.

Table 2
Summary of corrected SBE43 oxygen data from oxygen-depleted waters.

Cast ID	Depth interval, (M) ^a	Acquisition duration, s ^b	Mean concentration ^c , $\mu\text{mol kg}^{-1}$	Standard deviation, $\mu\text{mol kg}^{-1}$
<i>Casts for zero calibration with STOX data:</i>				
14.31	111–288	720	−0.015	0.025
14.47	91–282	654	0.011	0.024
14.73	149–265	756	0.025	0.029
14.74	101–335	709	−0.010	0.023
14.77	112–328	713	−0.012	0.020
All data 14.31–14.77		3552	0.000	0.029
<i>Casts without STOX data:</i>				
14.6	50–347	1104	−0.020	0.020
14.14	70–291	588	0.002	0.021
14.17	58–293	699	0.019	0.022
14.21	96–293	486	−0.012	0.034
14.96	134–315	534	−0.030	0.024
14.100	55–279	395	−0.026	0.023
14.122	242–317	290	−0.006	0.023
All data 14.6–14.122		4092	−0.010	0.029

^a Depth interval with oxygen depletion used for calculation. For casts with STOX oxygen data, the interval corresponds to the depths where oxygen was not detected with the STOX sensor. For casts without STOX oxygen data, the lower boundary was taken as the depth where the uncorrected SBE43 oxygen reading decreased below $1.7 \mu\text{mol kg}^{-1}$ during the upcast (corresponding to t_0 in Eq. (1)), and the upper boundary was defined as the first subsequent depth where the corrected SBE43 oxygen reading increased above 50 nmol kg^{-1} .

^b Duration of data acquisition within the depth range defined in the preceding column.

^c Corrected concentrations were derived by subtraction of a time-dependent zero-correction, which necessarily results in slightly negative means for some casts.

3.3. Respiration in the OMZ

The widespread depletion of oxygen to nanomolar concentrations or lower indicates that oxygen is efficiently respired to these low levels by the microbial community, while metazoan respiration must be strongly inhibited, even in those low-oxygen-adapted animals that are found in OMZs (Seibel, 2011). The case for active microbial respiration is supported by the apparent half-saturation coefficient for oxygen respiration of less than $0.02 \mu\text{mol kg}^{-1}$ reported for water from the Peruvian OMZ (Revsbech et al., 2009). Such kinetics imply the involvement of specialized respiratory oxidases with high oxygen affinity ($K_m < 0.01 \mu\text{mol kg}^{-1}$) as found in a variety of bacteria (Contreras et al., 1999). If oxygen consumption follows Michaelis–Menten kinetics, the time t to reach a given concentration C from an initial concentration C_0 can be calculated as $t = (C_0 - C + K_m \ln[C_0/C]) / V_{\max}$ (Dalsgaard and Bak, 1994). With a half saturation coefficient of $0.02 \mu\text{mol kg}^{-1}$ and typical mesopelagic rates of non-oxygen limited oxygen respiration ($V_{\max}$) of 0.02 – $0.05 \mu\text{mol kg}^{-1} \text{ d}^{-1}$ (Aristegui et al., 2005), oxygen would be depleted from the detection limit of the conventional sensor of $0.09 \mu\text{mol kg}^{-1}$ to $0.01 \mu\text{mol kg}^{-1}$ within 2–6 days and to $0.001 \mu\text{mol kg}^{-1}$ in 3–8 days, which is short relative to the residence time of the ESSW (Section 3.2). This is a conservative estimate because respiration rates in the region are likely above average for mesopelagic waters due to the high productivity. Thus, while mixing-events or intrusions may occasionally introduce oxygen into the OMZ core, as indicated by our finding of 10 – 50 nmol kg^{-1} oxygen at one station off Peru (Fig. 3(b)), it is not likely that oxygen persists at concentrations between the detection limits of the two methods used here (0.01 – $0.09 \mu\text{mol kg}^{-1}$), but rather that it is depleted to the limit of microbial respiration, which is probably in the picomolar range or lower.

A tight coupling is expected between the oxygen dependence of aerobic respiration and the onset of dissimilatory nitrate reduction, the first step in anaerobic respiration with nitrogen compounds (Devol, 1978). During our sampling, nitrate was present at concentrations greater than $10 \mu\text{mol kg}^{-1}$ throughout the OMZ while nitrite accumulated to micromolar levels in the OMZ core, in accordance with previous observations (Wooster et al., 1965; Fiadeiro and Strickland, 1968; Silva et al., 2009), with maximum concentrations increasing from north to south and reaching $10 \mu\text{mol kg}^{-1}$ at 20°S . We only observed the accumulation of nitrite above $0.5 \mu\text{mol kg}^{-1}$ when oxygen was undetectable with the SBE43 sensor, and at oxygen concentrations less than $0.05 \mu\text{mol kg}^{-1}$ where STOX sensor data were available (Fig. 7). This oxygen threshold for the secondary nitrite maximum is one to two orders of magnitude lower than thresholds of 1 – $4.5 \mu\text{mol kg}^{-1}$ previously estimated in large OMZ surveys with the same approach (Cline and Richards, 1972; Codispoti and Christensen, 1985; Morrison et al., 1999). The difference can be attributed to the improved sensitivity of oxygen determination since those studies placed the threshold of nitrite accumulation near the detection limit of their oxygen analysis. Although the mutual exclusion of oxygen and the secondary nitrite maximum in the OMZ reflects only the net outcome of interactions between aerobic and anaerobic processes, it has important implications for the interactions of oxygen and nitrogen transformations. It confirms that nitrate reduction rather than ammonium oxidation is the source of the secondary nitrite maximum, because the build-up of nitrite occurs in the absence of oxygen, both along the vertical gradients and along the path of the ESSW. The relationship between oxygen and nitrite also implies that nitrite oxidation is highly efficient at nanomolar oxygen concentrations, consuming any nitrite formed from ammonium oxidation or mixed in from the adjacent OMZ core. This is consistent with direct observations of nitrite oxidation in incubations of OMZ water at very low oxygen concentrations (Lipschultz et al., 1990; Füssel et al., in press). In principle, other nitrite-consuming processes such as denitrification and anammox could also be active at low oxygen levels (Fariás et al., 2009; Jensen et al., 2008), but they are less likely to explain the disappearance of nitrite

Fig. 7. Relative distribution of oxygen and nitrite in the core and oxycline of the oxygen minimum zone. Filled circles represent oxygen concentrations determined with STOX oxygen sensors with standard deviation of replicates ($n=3$ – 4) and open circles represent concentrations from a conventional sensor after recalibration. Oxygen was measured in situ at fixed depth while the water samplers were allowed to equilibrate with the surrounding water. Nitrite concentrations greater than $0.5 \mu\text{mol kg}^{-1}$ were only found at oxygen concentrations below $0.05 \mu\text{mol kg}^{-1}$ except for one sample containing $6.6 \mu\text{mol kg}^{-1}$ nitrite at $0.4 \pm 0.5 \mu\text{mol kg}^{-1}$ oxygen. In this case, sampled at 30 m depth, oxygen fluctuated rapidly from below 0.05 to above $1 \mu\text{mol kg}^{-1}$ due to water movement, and fluctuations were likely too fast to equilibrate with water inside the water sampler.

with the appearance of oxygen, as they appear more sensitive to oxygen than the nitrite-producing pathways (Kalvelage et al., 2011). Mixing events must occasionally bring higher concentrations of oxygen and nitrite together, but such events were too rare to be caught in our survey. This further implies that elevated nitrite levels are a good indicator of complete oxygen depletion in the OMZ, and thus, that the volume of oxygen-depleted water in the Eastern South Pacific ($<0.09 \mu\text{mol kg}^{-1}$) may be as large as $2 \times 10^{14} \text{ m}^3$, the volume occupied by the secondary nitrite maximum (Paulmier and Ruiz-Pino, 2009), which is eight times the $2.4 \times 10^{13} \text{ m}^3$ estimated above.

The high efficiency of oxygen respiration at oxygen concentrations in the low nanomolar range inferred here, suggests that aerobes would efficiently outcompete anaerobic nitrogen metabolisms under steady state conditions in this oxygen range (see also discussion by Codispoti et al., 2005). Since both denitrification and anammox utilize nitrite, and since N_2 production in the Eastern South Pacific OMZ has only been detected experimentally at nitrite concentrations greater than $0.5 \mu\text{mol kg}^{-1}$ (Thamdrup et al., 2006; Lam et al., 2009), the relative distribution of oxygen and nitrite (Fig. 7) further suggests that N_2 production in this system may be restricted to fully oxygen-depleted waters or water with a recent history of anoxia. This, however, needs verification from detailed investigations of the effect of nanomolar oxygen on individual nitrogen-transforming processes and their interactions.

4. Conclusions and perspectives

Our results define sharp limits to the influence of oxygen on biological and biogeochemical processes in the Eastern South Pacific OMZ. The absence of detectable oxygen in the OMZ core along more than 1000 km of our cruise track indicates that a large volume of the OMZ core is functionally anoxic through extended periods of time. It is not possible to demonstrate anoxia, the absence of oxygen, directly because any oxygen assay will have some detection limit, but with oxygen depleted to low nanomolar or even picomolar levels, and given a residence time of several months for the water in the OMZ core, oxygen cannot be of sustained significance in biological metabolisms or other major biogeochemical processes, which justifies our definition of the core as being functionally anoxic. Because anoxia cannot be proven directly, and given the relatively high detection limits of conventional oxygen assays, the accumulation of hydrogen sulfide has previously been used as an indicator of anoxic conditions (Richards, 1965). Hydrogen sulfide is only rarely detected in pelagic OMZs but this appears to be due to efficient oxidation coupled to nitrate or nitrite reduction, rather than to the lack of production, as active sulfate reduction has been detected in the OMZ core and sulfide-oxidizers are abundant there (Stevens and Ulloa, 2008; Canfield et al., 2010). Instead, our results suggest that the accumulation of more than $0.5 \mu\text{mol kg}^{-1}$ nitrite is a robust indicator of oxygen depletion to the low nanomolar range, at least in the Eastern South Pacific.

While we argue that anoxia is a normal phenomenon, the detection at one location of $10\text{--}50 \text{ nmol kg}^{-1}$ oxygen associated with a disturbance of the typical stratification through most of the OMZ core (Fig. 3(b) and Fig. 4), emphasizes that such events may also be important in the OMZ system. This calls for investigation of the frequency of disturbances and their associated oxygen dynamics. Also the low but highly fluctuating oxygen concentrations with thin layers of complete depletion observed above the OMZ core off Peru (Figs. 3–5) indicate a highly dynamic oxygen regime with the potential for coupling of aerobic and anaerobic processes, depending on the temporal response of the processes

to changes in oxygen availability. Investigations of these issues should focus on oxygen in the nanomolar range, which is a great challenge both analytically and experimentally due to the risk of contamination with oxygen from the atmosphere (De Brabandere et al., 2012).

Our measurements indicate that aerobic processes proceed efficiently to low nanomolar oxygen concentrations, which suggests that the anaerobic processes that lead to N_2 production in the OMZ may be competitively restricted to much lower oxygen levels than previously assumed. This does not exclude N_2 production in the presence of small amounts of oxygen in dynamic systems where active anaerobic populations are mixed into oxic waters (Jensen et al., 2008; Kalvelage et al., 2011). Also, a unique oxygen threshold for anaerobic processes may not be applicable across all OMZ waters, because the sensitivity to oxygen may vary among processes and be influenced by factors such as the availability of reduced substrate, and because organic aggregates may harbour microniches of variable size depending on the bulk oxygen concentration (Ploug, 2001). Still, the discrepancy between our results and the anaerobic thresholds of $0.7\text{--}20 \mu\text{mol L}^{-1}$ oxygen used so far in biogeochemical budgets and models of OMZs (see Karstensen et al., 2008; Paulmier Ruiz-Pino, 2009) is remarkable. A thorough revision of this important parameter is required and is particularly pertinent in view of the forecasted changes in oceanic oxygen concentrations and the burgeoning research in OMZs and marine dead zones. Oxygen determination in the low nanomolar range is the key to progress for in situ measurements and for detailed physiological studies in the laboratory.

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