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The OMZ and nutrients features as a signature of interannual and low frequency variability off the peruvian upwelling system

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Abstract

The last years, the Humboldt Current Upwelling Ecosystem and particularly the Northern component off Peru, was a natural scenario for several studies and a "hot spot" for scientists around the world because of their unique characteristics: (1) one of the bigger catch productivity, (2) one of the shallowest, intense and acidic Oxygen Minimum Zone (OMZ), (3) one of the intense nitrogen lost areas and anammox activity, and (4) one of the strongest interannual variability associated with the Equatorial remote forcing. In this context, we examined the oceanographic and biogeochemical variability associated with the OMZ off central Peru, from a monthly time-series (1996–2009) recorded off Callao (12°02′ S). Both, physical and chemical time series exhibit a significant temporal variability, with intense interannual El Niño effects in the deepening of the OMZ distribution and nutrients dynamic but also intraseasonal activity by the influence of the Equatorial Kelvin Wave (IEKW). The chemical time series indicate after 2002 year higher frequency variability in phase with the increase of the IEKW, particularly with the second mode activity. We present evidences that the IEKW appear to modulate the distribution and intensity of the OMZ in the area and in consequence an impact on the chemical structure and biogeochemical activity. The data suggest that the remote forcing could be strongest not only at interannual but also at lower temporal frequencies changing the seasonal signature of upwelling systems.

1 Introduction

The upwelling region off Peru hosts a complex biogeochemical system that is unique for at least two reasons. First it is embedded into a permanent, very shallow and intense Oxygen Minimum Zone (OMZ) of the tropical eastern south Pacific (Gutiérrez et al., 2008); and second it is exhibits a significant variability at a different time scales, in particular at inter-annual associated to the impact of Equatorial Kelvin waves and the El Niño–Sothern Oscillation, ENSO (Chavez et al., 2008).

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The OMZ is generated by the combination of high productivity, determining an oxygen demand during organic matter remineralization, and the sluggish ventilation in the region (Wyrtki, 1962; Helly and Levin, 2004). It is wide in the vertical extension (∼ 500 m) intense (< 22 µmol kg^{-1}), and at some latitudes the upper boundary could be very shallow (25–50 m) intersecting the euphotic zone and impinging the continental shelf (Morales et al., 1999; Schneider et al., 2006; Fuenzalida et al., 2009; Paulmier and Ruiz, 2009; Ulloa and Pantoja, 2009). The OMZ off Perú is associated with the presence of nutrient-rich Equatorial Subsurface Waters (ESSW) that is transported poleward by the Peru–Chile Undercurrent (PCU) (Strub et al., 1998; Fuenzalida et al., 2009; Silva et al., 2009). This water fertilizes the surface during the upwelling events that occurs around all the year with maximum intensity during winter periods out of phase with the maximum chlorophyll *a* values (Echevin et al., 2008; Chavez and Messié, 2009; Gutiérrez et al., 2011).

The OMZs play a relevant role in the global biogeochemical activity of the ocean, as an ocean–atmosphere source of CO_2, as was identified off Perú (Friederich et al., 2008) and of N_2O (Paulmier et al., 2008; Farías et al., 2009a, b) with a positive feedback on global warming. This area represented one-third of the total fixed nitrogen loss in the ocean (Codispoti and Packard, 1980; Codispoti et al., 2001), in the last years associated with anammox activity (Hammersley et al., 2007; Lam et al., 2009; Lam and Kuypers, 2011). The position, strength and thickness of the eastern south pacific OMZ can be greatly modified by local and/or remote forcing at low frequencies (e.g. interannual time scales, Morales et al., 1999; Gutiérrez et al., 2008). During ENSO, changes in the equatorial dynamics extend to the coast of Peru which behaves as an extension of the equatorial wave guide (Clarke and van Gorder, 1994). Strong El Niño (EN) events, like 1997–1998 EN, affect the circulation and water masses distribution that determine the deepening of the OMZ below 100 m depth and large oxygenations events in the water column and over the sediments along the Chilean and Peruvian coasts (Morales et al., 1999; Sánchez et al., 1999; Gutiérrez et al., 2008). Helly and Levin (2004) report 60 % reduction in the sea floor area influenced by the eastern south

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Pacific OMZ off Peru and northern Chile during EN years. Additionally, coastal-trapped Kelvin waves can modulate at sub-seasonal scale the vertical structure of the physical parameters in the water column (e.g. the vertical temperature (Blanco et al., 2002), productivity (Echevin et al., 2014) and dissolved oxygen conditions; Morales et al., 1999; Gutiérrez et al., 2008).

The recent decades, ENSO has experienced significant changes in its variability (Lee and McPhaden, 2010; Takahashi et al., 2011) that may be attributed to some extent to the impact of global warming (Yeh et al., 2009). Recent investigations show another pattern, becoming the second dominant mode of interannual variability developed mostly in the central Pacific known as El Niño Modoki (Ashok et al., 2007; Ashok and Yamagata, 2009; Takahashi et al., 2011). This has clear implications for the variability of the water mass properties off Peru considering that El Niño Modoki is not associated with the advection of warm waters in the eastern tropical Pacific and off the Peruvian coast compared to the so-called "canonical" El Niño (Dewitte et al., 2012). In addition, the persistence of warm anomalies in the central Pacific (i.e. over the warm pool region) is propitious for the enhancement of the intraseasonal tropical atmospheric variability, in particular the Madden and Julian Oscillation (Madden and Julian, 1971, 1972, 1994). The latter can force energetic intraseasonal Kelvin waves (Roundy and Kiladis, 2006) that in turn may influence the upwelling variability off Peru (Dewitte et al., 2011) and also the OMZ and nutrients features.

The last decade is therefore a peculiar period with respect of the equatorial (Dewitte et al., 2009, 2011) remote forcing characteristics (Dewitte et al., 2012; Gushchina and Dewitte, 2012) and the impacts of these onto the biogeochemical properties off the Peruvian coast. In this study we take advantage of a long term time series of oxygen and nutrients off central Peru in order to infer potential biogeochemical scenarios in connection with the equatorial variability over the last decades. These historic data collected on a monthly basis by the Chemical Oceanography Research Unit of the Marine Research Institute of Peru (Imarpe) provide a unique opportunity to explore

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the low frequency variability of the OMZ and their implications for the biogeochemical activity in the area.

2 Methods

2.1 Study area

A monthly time series (1996–2009) of vertical profiles of temperature, salinity, oxygen and nutrients (nitrate, nitrite, phosphate and silicate) off Callao (12°02′ S) at 20 nm from the coast (St. 4, 145 m) were standardized with their annual cycle in order to explore the interannual variability in the study area (Fig. 1). The Callao area is characterized by an intense upwelling regime, maximum in winter periods, high primary productivity rates in spring-summer and the presence of nitrate-rich and oxygen deficient sub-surface waters called in the area as Cold Coastal Waters (Zuta and Guillén, 1970; Graco et al., 2007). The Cold Coastal Waters correspond to the Equatorial Subsurface Waters mass (Strub et al., 1998; Silva et al., 2009).

2.2 Water column profiles

Water samples were collected monthly with Niskin bottles during cruises of the IMARPE r/v *IMARPE VIII*, *SNP-1* and *SNP-2*. Temperature was measured by inversion thermometer through 2001 and by CTD (Seabird SBE 19+) from 2002. Salinity was measured by salinometer through 2001 and by CTD from 2002.

Dissolved oxygen and nutrients were measured at standard depths (0, 10, 30, 50, 75, 100 m). Dissolved oxygen was determined by a modified Winkler method (Grasshoff et al., 1999), with a precision of 5 $\mu mol\,kg^{-1}$ and large errors in values lowers than 10 $\mu mol\,kg^{-1}$. Nutrients samples (nitrate, nitrite, phosphate and silicate) were stored frozen until analyses using standard colorimetric techniques, the precision for nitrate analysis was ±0.5 µM, for nitrite ±0.08 µM, for phosphate ±0.03 µM and ±0.25 µM for silicate (Parsons et al., 1984).

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The fixed nitrogen deficit (Ndef) was determined by the formula:

$$\mathrm{Ndef} = 12.6 \times [\mathrm{PO_4^{3-}}] - ([\mathrm{NO_3^-}] \times [\mathrm{NO_2^-}])$$

Where the constant 12.6 is the empirically-determined N : P ratio of organic matter produced in these waters (Codispoti and Packard, 1980). Positive values indicate deficit of the nutrient.

The OMZ was defined as the area with concentrations lowers than 22.3 µmol kg^{-1}, this concentration was considered the upper boundary of the OMZ as was considered in several publications (Schneider et al., 2006; Fuenzalida et al., 2009; Ulloa and Pantoja, 2009).

2.3 Statistical analysis of time series

Linear interpolation was utilized for complete minor gaps into the 1996–2009 time series. The monthly anomalies were calculated as the difference between the original data and the mean seasonal cycle calculated over the time series, normalized by the standard deviation. To compare variances, the time-series were analyzed with discrete wavelets (Torrence and Compo, 1998) to represent temporal changes in spectra. To summarize and comprise the variability on subsurface and bottom waters, also the first Principal Component (PC1) (Emery and Thomson, 1998) of the raw time series was calculated and used as an index of the subsurface variability. The simple empirical orthogonal Function (EOF) analysis applied to the normalized (by standard deviation) monthly time series of physical (temperature and salinity), chemical (oxygen, nutrients) and nitrogen (nitrate, nitrite and N deficit) data sets was performed at different depths in order to summarize the main signal of physical chemical co-variability by principal component per each level of depth. The Pearson correlation coefficient (r) was calculated between series; in addition, the cross correlation between chemical and physical time series with –1, 0,+1 lags was run in order to explore the lag coupling between time series.

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2.4 Intraseasonal equatorial kelvin waves (IEKW)

To diagnose the Intraseasonal Equatorial Kelvin Wave (IEKW) activity near the coast, we derived estimates of the first and second baroclinic modes of Kelvin (IEKW_1 and IEKW_2) wave amplitudes of the sea level height (in cm) at 90° W from the SODA oceanic Reanalysis (Carton and Giese, 2008). The method consists in projecting the pressure and current from SODA onto the theoretical vertical mode functions obtained from the vertical mode decomposition of the mean stratification. Kelvin wave amplitude is then obtained by projecting the results onto the horizontal modes. The method has been shown successful in separating first and second baroclinic waves (Dewitte et al., 1999, 2008) that propagate a different phase speed and impact the Peru coast in a very specific way. In particular due to the sloping thermocline from west to east along the equator, the second baroclinic mode Kelvin wave is more energetic and influential on the upwelling variability off the Peruvian coast (Dewitte et al., 2011, 2012). In addition the global spectrum analysis was performed for the IEKW activity 1 and 2 and for the different physical and chemical variables.

3 Results

3.1 Oceanographic dynamics off central Peru (Callao, 1996–2009)

Vertical distribution time series of temperature (a), salinity (b) and density (c) off Callao (St. 4) during 1996–2009 years are shown in Fig. 2. The data set collected in this coastal and shallow station shows a water column with strong interannual signal, with significant changes in the 15 °C isotherm depth. Here the15 °C isotherm depth is considering as a proxy of the lower limit of the thermocline position, from 20 to more than 100 m like during the 1997–1998 El Niño.

Under "normal" conditions, the subsurface waters of the area were characterized by a dominant presence of Equatorial Subsurface Waters (ESSW), with low temperatures (< 15 °C) and salinities (34.8–35.1). The vertical distribution of 26 kg m^{-3} isopycn, as show the Fig. 2c, was coincident with the 15 °C isotherm. Maximum temperatures at surface (up to 22 °C, Fig. 2a) occurred during summer and spring periods, when a shallow mixed layer occurs (up to 20 m water depth). The climatology of the 15 °C isotherm depth (Z_15) suggests a semi-annual pattern (Fig. 4a), shallower in early fall and spring, deeper in winter and slightly deeper in late summer.

A strong deepening in the 15 °C isotherm was observed (Fig. 2a and see outliers at Fig. 4a) from the end of 1997 until the beginning of 1998, as a consequence of Subtropical Surface Waters (SSW) penetration into the coast determining the presence of warm and salty (> 35.2) conditions (Fig. 2b). This corresponds to the impact of the intense 1997–1998 El Niño that switch the coastal upwelling characteristics during almost one year. Note that the disappearance of the 15 °C isotherm in the first 100 m took place in the early 1997 (around April) well ahead the El Niño peak phase (around November).

After the 1997–1998 El Niño the 15° isotherm depth presented lower variability. We observe a slight deepening at the beginning of 2002, 2005, during winter of 2006, 2008 and 2009 that was coincident with weak or moderate El Niño conditions and could indicate the impact of the Intraseasonal Equatorial Kelvin Waves activity (IEKW, see Sect. 3.5). The large variations in the mean depth of the 15 °C and the 26 kg m^{-3} isopycn were significant correlated (R^2 0.70, $v - p < 0.01$).

The first EOF mode of the physical component (PC1, T°, Salinity) explains 84.5 % of the total variance subsurface analysis (Fig. 6a). This mode account of fluctuations associated with the interannual variability, particularly the influence of strong El Niño period.

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3.2 The dissolved oxygen regime and the oxygen minimum zone (OMZ) variability (Callao, 1996–2009)

The dissolved oxygen (DO) distribution shows a similar pattern than the oceanographic parameter with a strong interannual signal, particularly during 1997–1998 El Niño years and also after the event that can overlap the seasonal pattern (Figs. 3 and 4). Here the iso-oxygen of 44.6 µmol kg^{-1} is used as a proxy of the mean position of the oxycline and of the 22.3 µmol kg^{-1} iso-oxygen as the OMZ's upper boundary position. A shallow position (20–40 m) of the oxycline (iso-oxygen of 44.6 µmol kg^{-1}) and of OMZ (22.3 µmol kg^{-1} iso-oxygen) were observed under an active upwelling of the Equatorial Subsurface Waters (ESSW) in the area, as during 1999–2001 period. On average, this condition is characteristic during summer-fall periods (see the climatological annual pattern, Fig. 4b and c), but also in spring time suggesting a semi-annual pattern. During these seasons the intensification of poor oxygen waters can intercept the euphotic layer and also the continental shelf, favoring suboxic and also anoxic conditions in the underlying surface sediments (O_2 < 8.9 µmol kg^{-1}, Fig. 3). During austral winter (July-August) the oxygen deficient waters are deepened (up to 70 m depth, Figs. 3 and 4) coincident with the moment of strongest winds and higher levels of turbulence.

At interannual scale, during the strong 1997–1998 El Niño, a significant deepening of the oxycline and the OMZ upper boundary occurred, when the oxygenated Subtropical Surface Waters (SSW) occupied the water column down to at least 100 m depth. An interesting feature arising from the temporal OMZ distribution, besides the strong amplitude of the fluctuation associated to the 1997–1998 El Niño, is the relatively large interannual/intraseasonal variability since 2002 (see 2006, 2008, 2009, Figs. 3b and 4c). This variability is in some periods in an opposite phase of the physical conditions, as the 15 °C isotherm. Before 2002, the oxycline and the OMZ's upper boundary present a significant correlation with the 15 °C isotherm (R^2 0.59, $v-p < 0.01$ and R^2 0.51, $v-p < 0.01$ respectively), after the 2002, we observe frequently a decoupling between this variables (R^2 0.20, $v-p < 0.01$ and R^2 0.19, $v-p < 0.01$ respectively).

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The oxycline and the upper boundary of the OMZ appear less correlated since 2002 (R^2 0.79, $v-p < 0.01$ before 2002 and R^2 0.51, $v-p < 0.01$ since 2002).

3.3 Nutrients and biogeochemical activity at interannual and low frequency variability (Callao, 1996–2009)

Time series of nitrate, nitrite, silicate and phosphorus vertical distribution off Callao (St. 4) are shown in Fig. 5. Nitrate and nitrite concentrations ranged from ca. 0.0 to 27.0 μmol L^{-1} and ca. 0.2 to 9.0 μmol L^{-1} values respectively. Lower nitrate values are present at surface and bottom waters, particularly during summer and fall periods, while maximum nitrites appear at subsurface waters in an opposite relationship with nitrates. During winter periods maximum nitrate concentrations characterize the water column (> 15 μmol L^{-1}), coincident with the period of maximum upwelling intensities. The vertical distribution of silicate and phosphate exhibit a similar pattern than nitrate (Fig. 5c and d).

A strong interannual signal with lower nitrate concentrations (< 10 μmol L^{-1}) coincident with minimum an even zero nitrite values and low silicates and phosphates (< 10 and 1 μmol L^{-1} respectively) over the entire water column during 1997–1998 El Niño period (Fig. 5a and b).

Between 1999 and 2001 the nitrate concentrations were also lower than 10 μmol L^{-1} on average, but maximum nitrite subsurface values (up to 9 μmol L^{-1}) were coincident with the intense OMZ development and the shallow thermocline. Silicate depletion was observed at surface waters, while phosphate in general appears as a non-limiting nutrient at surface waters. At subsurface high silicates (> 25 μmol L^{-1}) and phosphates (3 μmol L^{-1}) concentrations were observed.

After 2002, the water column was dominated by the highest nitrate concentrations (> 20 μmol L^{-1}), while nitrite concentrations were significantly reduced (< 1 μmol L^{-1}) before 2006 and increase again during 2006, 2007, and 2009 summers. The seasonal signal in the nitrate time series is not evident because of the over imposed strong interannual signal and also the intraseasonal imprint (see Sect. 3.5). A decrease on

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the average subsurface silicate concentration was observed before 2006, coincident with the presence of low nitrite and high nitrates (Fig. 5d).

The EOF of the chemical component (oxygen, nutrients at subsurface depths; 50 and 90 m), show a variability explained by two dominant modes, 50 % PC1 and 30 % PC2 (Fig. 6b). The PC2 appears to be connected with the intraseasonal variability that is increasing after 2002 and appear associated by the activity of the IEKW, particularly the IEKW_2 (see Sect. 3.5).

In order to explore some biogeochemical activity related with the nitrogen cycle and the OMZ variability off Callao, we calculate the nitrate deficits values (Ndef) in the water column as the difference between the nitrate concentrations expected if there were no denitrification obtained by the phosphate concentrations and the observed nitrate plus nitrite concentrations (Fig. 7). Ndef values ranged from negative (–5 $\mu mol\,L^{-1}$) that indicate low nitrate consumption up to 40 $\mu mol\,L^{-1}$ in a very deficient conditions. The Ndef, particularly at subsurface depths, show a clear interannual signal with minimum values (zero-negative) during the 1997–1998 El Niño coincident with strong oxygenated conditions (Fig. 3). The opposite occurs between 1999 and 2001 years, when maximum Ndef (30–40 $\mu mol\,L^{-1}$) occur under a shallow and well developed OMZ. The nitrate reduction in this period was evident in the high nitrite subsurface accumulation (Fig. 5).

After 2002, we observe a Ndef water column conditions highly variable coincident with the variability in the OMZ distribution. Lower values were observed before 2006 and then periods with strong deficient conditions coincident with the same pattern observed in the nutrients distribution. Ndef at subsurface (50 and 90 m depth) was significantly correlated with the 15 °C isotherm (R^2 0.53, $v-p < 0.05$) and with the OMZ (R^2 0.44, $v-p < 0.05$).

3.4 Remotely-driven temporal variability, physical vs. biogeochemical factors impact on the OMZ

We document the evolution of the Intraseasonal Equatorial Kelvin Wave (IEKW) activity of the first and second mode during the 1996–2009 period in order to relate the

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temporal variability of the physical and biogeochemical parameters described above to the remote equatorial forcing. We present the evolution of the amplitude of the first and second baroclinic modes (IEKW_1 and IEKW_2) at 90° W in terms of anomalies (Fig. 8a and b). It is assumed that waves with amplitude larger than one standard deviation over the period (see horizontal lines in Fig. 8a and b) are downwelling Kelvin waves whereas when the amplitude is more negative than −1 standard deviation, the wave is an upwelling Kelvin wave (Dewitte et al., 1999, 2008). Therefore upcoming coastal-trapped downwelling (upwelling) waves will tend to reduce (increase) wind-driven coastal upwelling near Callao.

Our data first reveals that the IEKW_2 mode is delayed by 1 month compared to the first baroclinic mode (IEKW_1) consistently with the different in phase speed of the waves and their propagation from the central equatorial Pacific. The maximum correlation between both time series was before 2000 (r 0.71, $v - p < 0.05$). Over 2000–2009 period the correlation was significantly lower (r 0.53, $v - p < 0.05$). The ratio between downwelling (upwelling) Kelvin wave of the second baroclinic mode periods and downwelling (upwelling) Kelvin wave of the first baroclinic mode periods is 0.46 (2.13). This indicates that the second mode favours upwelling events whereas the first baroclinic is more associated to downwelling events near the coast. The skewness coefficient indicates that IEKW activity changed before and after 2000. The mean anomaly was more positive before 2000 year, 1.41 (IEKW_1) and 1.57 (IEKW_2). Also the global wavelet spectra analyses show that IEKW_2 is associated to lower frequencies timescales compared to IEKW_1 (Fig. 8a and b).

Figure 8c and d shows the anomalies under the same period (1996–2009) for the 15 °C depth (Z_15 °C) and the upper boundary of the OMZ depth (Z_ZMO). Higher anomalies of the IEKW than 0 (Fig. 8a and b) are associated to a deepening of the 15 °C isotherm (< 0), as was observed during the 1997–1998 El Niño, during 2002 Weak El Niño and also during 2006 and 2008 warm periods. During these periods the IEKW mode 1 and 2 activity are in phase with comparable amplitude and the Z_15 °C and the Z_ZMO are in phase but in an opposite way.

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The global wavelet spectrum analysis for the IEKW_1 and 2 revealed period band dominance of 2–6 yr^{-1} (interannual activity), but also in 180 days (6 months)–90 days (3 months) (Fig. 8f and g). The intraseasonal signal appears clearly in the Z_15 °C, Z_ZMO and N_def50 in agreement with the IEKW activity (Fig. 8). The IEKW_1 and 2 are highly correlated with the physical and chemical component, but we find that the IEKW_2 is more strong and negatively correlated with the Z_15 °C and Z_ZMO (r −0.69, −0.52 respectively, $v-p < 0.05$) than the IEKW_1 (r −0.35, −0.21 respectively, $v-p < 0.05$).

Before 2000, the IEKW_1 activity was more negative than between 2000–2009 (−0.44 and 0.11 respectively), in an opposite way that the IEKW_2 (−0.37 vs. −0.89). After 2000 a different pattern in the 1 and 2 mode activity of the IEKW occurs, leading to an increasing frequency variability. This appear to have implications for the biogeochemical activity at subsurface, as shown by the evolution of the nitrate deficit anomalies (N_def50, Fig. 8e), significant correlated with the IEKW_2 (r −0.44, $p < 0.05$).

4 Discussion

4.1 The OMZ and nutrients regime as a signature of interannual and low frequency variability of the Peruvian upwelling system

The region of Callao (12° S) have been identified as one of the major upwelling cells off central Peru (Rojas de Mendiola, 1981) with a subsurface well developed OMZ (< 22.3 O_2 µmol L^{-1}) (Wooster and Gilmartin, 1961; Zuta and Guillén, 1970). The chemical time series off Callao, dissolved oxygen and nutrients, presented in this study, represent a valuable observed data set for characterizing the intensity and variability of the biogeochemical component of the OMZ and the coupling between the local and the remote forcing (Purca, 2005; Gutiérrez et al., 2008). Most of the studies on the impact of El Niño events have focused in the depth of the thermocline and/or the sea level fluctuations (Hormazábal et al., 2001; Montecino et al., 2003). Some others have doc-

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umented the remotely-driven effects of El Niño and coastal trapped waves on the OMZ boundaries off Chile and off Peru (Escribano et al., 2004; Hormazábal et al., 2006; Montecino et al., 2003; Gutiérrez et al., 2008; Morales et al., 1999). Only a few time series of chemical data, nutrients, along the Peruvian coast have been published exploring the behavior of interannual changes vs. remote forcing (Calienes and Guillén, 1981; Flores et al., 2006; Guillén and Izaguirre de Rondán, 1973; Guillén et al., 1989; Ledesma et al., 2006).

The OMZs are associated with areas of intense organic matter remineralization, oxygen consumption and nitrogen loss (Helly and Levin, 2004). In this context, the OMZ variability in terms of distribution and intensity has a direct impact on the biogeochemical processes of the northern component of the Humboldt upwelling system, because oxygen is a key factor in biogeochemical cycles, particularly the carbon and nitrogen processes (e.g. Codispoti et al., 2001; Lam and Kuypers, 2011) but also as a control factor in the distribution of organisms (Arntz et al., 1991; Bertrand et al., 2010; Criales et al., 2006; Díaz and Rosenberg, 2008; Ekau et al., 2010; Escribano, 2006; Levin et al., 2002; Stramma et al., 2010). Our results show that between 1996 and 2009 in the central area of Peru the position and intensity of the OMZ present a semianual cycle with a marked modulation at interannual frequency. A shoaling of the OMZ was particularly observed during summer/fall and early spring, up to < 50 m, which tends to coincide with the periods of highest levels of chlorophyll *a* and primary productivity rates in the area (Pennington et al., 2006; Echevin et al., 2008). During the austral winter the opposite was observed with a deepening of the OMZ ($>$ 40–50 m), under the occurrence of strong upwelling winds that could promote mixing and some oxygenation in the water column. Winter period present less oxygen consumption because of the lower availability of organic matter. Superimpose to the seasonal/semiannual variability stronger changes in the OMZ and in the nutrient conditions occur at interannual scales.

During the end of 1997 and the start of 1998, warmer, oxygenated poor-nutrient waters were dominant in the water column as is expected under the intrusion onshore of Subtropical Surface Waters (SSW) observed in the central area off Perú during El Niño

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events (Morón, 2000; Morón and Escudero, 1991). The disappearance of the 15 °C isotherm in the first 100 m took place in the early 1997 (around April) well ahead the El Niño peak phase (around November). This traduces the impact of the downwelling Kelvin waves that were triggered in December 1997 and March 1998 in the central Pacific (Dewitte et al., 2003). These waves deepened the coastal thermocline, initiating the anomalous conditions prior to the development of El Niño (Ramos et al., 2006). A significant correlation between the 15 °C isotherm and the OMZ upper boundary depth suggest the connection of the remote forcing in both the physical and the chemical pattern that evidence the poleward subsurface propagation of the coastal trapped waves from the equatorial region along the Peruvian continent. Previous works show the influences of the equator in the propagation of the sea level fluctuations reported in Chile by Enfield and Allen (1980), and also the strong influence between the poleward waves propagation and the OMZ distribution, with an apparent lag phase increasing from the equator to the south (Morales et al., 1999). The coastal trapped waves influence was reported in the Northern off Chile by Hormazábal et al. (2001) and was also recently observed onshore off Peru by Gutiérrez et al. (2008).

Under the 1999–2001, considered as a cold phase of the ENSO cycle, the water column off Callao was dominated by a shallow thermocline, pycnocline, OMZ and nutricline. Negative oxygen anomalies were dominant at subsurface waters off Callao. Codispoti et al. (1988) proposed a thermocline “overshoot” in the years following an El Niño event, and Guillén and Calienes (1981) suggest that cold anomalies can occur up to three years after an El Niño, as we observe in this work. The cold conditions of 1999–2001 were associated to the enhancement of the near-annual mode in the equatorial Pacific (An and Jin, 2004) which resulted in pulses of cold SST anomalies after the 1997–1998 El Niño. The shallow nutricline, and high phosphate and silicate concentrations suggest high productivity and an intense remineralization promoting a well-developed oxygen deficient waters and favorable conditions for nitrate reduction and nitrogen loss processes as evidence the low subsurface nitrate concentrations

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($< 10\,\mu mol\,L^{-1}$) and the high nitrate deficit and high nitrite accumulations off Callao ($> 5\,\mu mol\,L^{-1}$).

After 2002, there is a change in the relationship between the thermocline and the upper boundary of the OMZ, with an apparent decoupling between physical and biogeochemical forcing. Isolated oxygenation events take place that are not associated with changes in the thermocline and pycnocline, e.g. April of 2005. Under these conditions, high phosphate, silicate and nitrate and about zero nitrite values were characteristics, suggesting a lower nutrient recycling and a not significant nitrogen loss (low Ndef) in the system. These conditions agree with a less intense OMZ ($O_2 > 10\,\mu M$), and neutral to positive oxygen anomalies during this period suggest lower oxygen consumption in the water column (see below).

The physical PC1 indicate that 84.5 % of the variability between 1996 and 2009 off Callao, central Peru, could be explained by remote forcing and interannual changes. In the case of the chemical component 50 % is explained by the PC1 and the second mode (PC2) appear explain 30 %. This result is coincident with Gutiérrez et al. (2008), estimated that only 43 % of the temporal variability in the OMZ position is explained by the remote forcing and suggested that local physical and/or biogeochemical processes, as coastal upwelling, wind mixing and red tide blooms, which appear to increase in frequency and intensity in the last years (Delgado and Sánchez, 2012), could be important factors onshore that modulate the OMZ. In a recent work the geometry of the shelf appear also as a key factor in upwelling systems and in interaction with remote forcing help to explain changes of the seasonal and/or interannual variability of shelf hypoxia (Monteiro et al., 2011).

4.2 Potential biogeochemical scenarios under the influence of the IEKW_1 and IEKW_2 activity

The nutrients time series off Callao, in particular nitrite, put in evidence the modulation of the biogeochemistry activity by remote forcing from the Equatorial Pacific and the

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Equatorial Intraseasonal Kelvin Wave (IEKW) activity, at interannual, as under El Niño event, but also at intraseasonal time scale particularly since 2002. The first and second mode of the IEKW (IEKW_1 and IEKW_2) activity show a strong correspondence with the physic and chemistry of the area, in particular the intensity of the OMZ.

We proposed three Biogeochemical scenarios (BG) for the central Peruvian upwelling system associated with the physical and chemical variability from 1996 to 2009 under different IEKW activity patterns:

- BG1_EN, observed under strong El Niño conditions, as the 1997–1998 period. Under this scenario the IEKW_1 and 2 activities are in phase, both with positive and similar magnitudes, associated with strong downwelling conditions. The water column is dominated by warm, oxygenated and poor nutrients water masses. The physical forcing appears in phase with the biogeochemical activity. The oxygen deficient waters ($< 44.6\,\mu M$) disappear from the water column and there is a significant deepening in the nutricline ($> 80\,m$ depth). Similar conditions were reported off Peru under the 1982–1983 strong El Niño when Guillén et al. (1989) showed a significant deepening of the thermocline, oxycline and nutricline, and a general increase in oxygen concentration in the layers below the surface. These conditions appear not favorable for the development of an important primary productivity, because of a less nutrient availability in the surface layer and neither for an important nitrogen recycling, denitrification-anammox activity, as suggest low and even zero nitrite concentrations plus low nitrate deficit. The significant effect on denitrification in the eastern South Pacific Ocean remotely forced by the changes in the equatorial winds during El Niño (EN) was previously suggested by Codispoti et al. (1988) as a large-scale response to EN. A recent work on the continental shelf off Callao, show evidence for the first time that the interannual variability in the rates of denitrification and anammox processes, and show a significant decrease in the nitrogen loss processes under El Niño conditions coupled with a lower primary productivity and higher oxygenation under the shelf (Graco et al., 2008).

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- BG2_LN, observed under La Niña or cold periods conditions, as during 1999–2001. IEKW_1 and 2 modes are dominated by negative anomalies that indicate predominance of upwelling conditions associated with intensification of oxygen deficiency in the water column. The physical variables (thermocline) appear in phase with the oxycline and the OMZ's upper boundary position and also with the nitrate reduction and nitrogen loss processes. A co-occurrence of a shallow and intense deficient oxygen conditions (OMZ < 20 m depth) with low nitrate values ($< 10\,\mu$mol L^{-1}), subsurface nitrite maximum (up to 9 µmol L^{-1}) and high nitrogen deficit are signatures of an important biogeochemical activity, characterized by high organic matter remineralization coupled to an intense oxygen demand and strong nitrate reduction-denitrification/anammox processes. Secondary nitrite maximum with concentrations that exceed 6 µmol L^{-1} were described as a typical feature within suboxic layers (Deuser et al., 1978; Naqvi, 1991) and a trace waters with denitrification and potential areas as nitrogen sources to the atmosphere (Codispoti and Packard, 1980; Codispoti et al., 1986; Naqvi et al., 1994). Maximum nitrite concentrations (up to 10 µmol L^{-1}) has been found previously in the suboxic waters off Peru where an intense denitrification was recognized (Codispoti and Christensen, 1985; Codispoti et al., 1986), and recently an important anammox activity has been revealed (Hammersley et al., 2007; Lam et al., 2009; Lam and Kuypers, 2011). Secondary nitrite maximum also appear in the OMZ off Chile (Morales et al., 1996), where an intense nitrogen loss activity was reported at sediments (Thamdrup and Dalsgaard, 2002) and in the water column (e.g. Farías et al., 2009a; Thamdrup et al., 2006). Similar results were observed at other upwelling ecosystems as Benguela (Calvert and Price, 1971) and at the Eastern tropical South Pacific (Codispoti and Christensen, 1985; Tyrrell and Lucas, 2002).

- BG3_WCE, observed after 2002, under "episodic weak Warm and strong Cold Events" when an intense seasonal variability and a higher frequency of upwelling (downwelling) waves associated to IEKW activity. The IEKW_1 (IEKW_2) modes show positive (negative) anomalies in an opposite way, coincident with a higher frequency of El Niño weak events during the recent decade. The IEKW_1 and 2 mode suggest after 2002 an increase in the amplitude of downwelling and upwelling modes, respectively, that appear to modify the physical (e.g. temperature) structure but also the chemical component at subsurface waters. Conditions characterized by a less intense OMZ (oxygen > 10 µmol L^{-1}), higher nutrients (nitrate > 20 µmol L^{-1}), nitrite near zero values and low N deficit at the subsurface waters appears under "warm periods" as 2002, 2006, 2008, dominated by IEKW positive anomalies, associate with downwelling Kelvin wave and ventilation in the water column. The low nitrogen deficit and nutrients data suggest a low nitrogen recycling and low nitrogen loss in the area under this condition. In the opposite way, episodic "cold events", as in 2005, 2007 associated with negative anomalies of the IEKW favorable for upwelling conditions with a higher development of the OMZ and intense nitrogen recycling as suggest the high nitrogen deficit values.

The BG3-WCE appear as a combination of BG1 and BG2 in a higher frequency (intraseasonal signature) that could promote changes in the "normal seasonality" (warmer winters associated with Kelvin Wave activity) in the system determining the mismatch between the physical and the biogeochemical processes coupling and the response in the biogeochemical activity and also the biological communities in the system. These changes was also suggested in recent years at different upwelling systems (California; Bograd et al., 2008; Benguela, Monteiro, personal communication 2008) and could be associated with a change in the phytoplankton size and/or community structure, as was observed in California (Chavez, personal communication, 2015).

In addition, the changes since 2002 are also coincident with changes in El Niño "flavor" and a higher frequency of El Niño Modoki (Dewitte et al., 2012) that could have important implications for the long-term trend of the upwelling system off Peru but also for others upwelling systems. It is necessary to continue the obser-

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vations and include also others components of the system in order to confirm this hypothesis.

5 Conclusions

This study suggest a more complicate temporal variability of the OMZ and biogeochemical activity of the Peruvian upwelling system on intraseasonal to interannual scales connected with the local and remote forcing, particularly the IEKW activity over the last years. The data set presented in this paper cover contrasted episodes of interannual variability as an intense El Niño (1997–1998), La Niña (1999–2001) and an extended period of time with moderate warm and cold anomalies (2002–2009) connected with different patterns of IEKW activity of the first and the second mode. While the global trend in the open ocean appear to be an expansion of the oxygen deficient waters, particularly in the tropical oceans during the past 50 years, in the coastal areas many questions remain open related with short term temporal variability and the onshore-offshore physical and biogeochemical coupling dynamics that regulate in a complex interplay the intensity and distribution of the OMZ and can determine different biogeochemical scenarios with a potential impact for the coastal human communities.

Author contributions. The study was designed by M. Graco. O. Morón, G. Flores and J. Ledesma carried out the data out field work, sample preparation and analysis. S. Purca, B. Dewitte and C. Castro perform the data analysis including the statistical analysis. All co-authors contributed to data interpretation and general discussion. M. Graco wrote the manuscript with contribution from all the co-authors.

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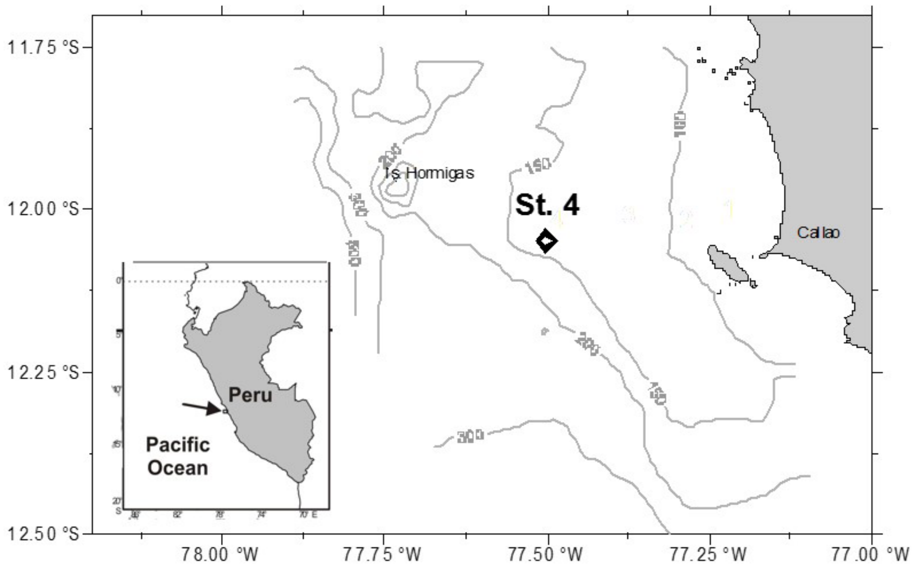

Figure 1. Location of sampling site Station (St.) 4 (20 nm, 145 m depth) in the upwelling ecosystem off central Peru, Callao (12° S).

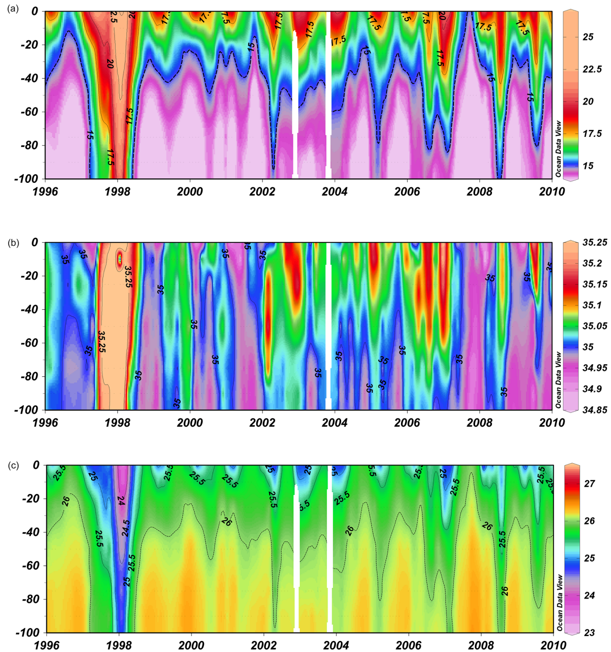

Figure 2. Characterization of the water column in terms of temperature **(a)**, salinity **(b)** and density values **(c)** distribution during the 1996–2009 time series.

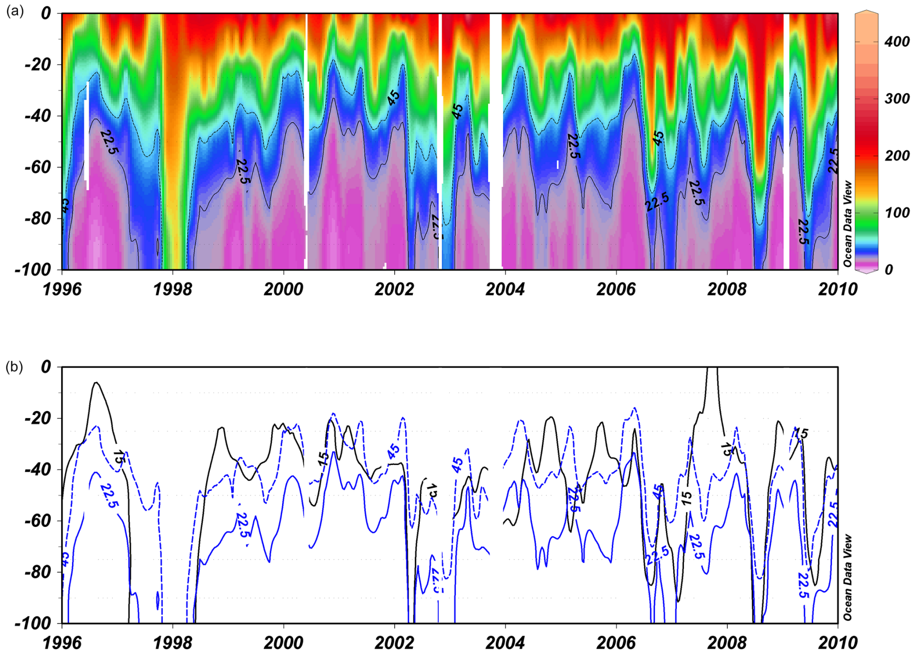

Figure 3. Vertical distribution of dissolved oxygen **(a)** and the depth of the 15 °C isotherm, the oxycline (44.6 µmol L^{-1}) and the upper boundary of the OMZ (22.3 µmol L^{-1}) **(b)** during the 1996–2009 time series.

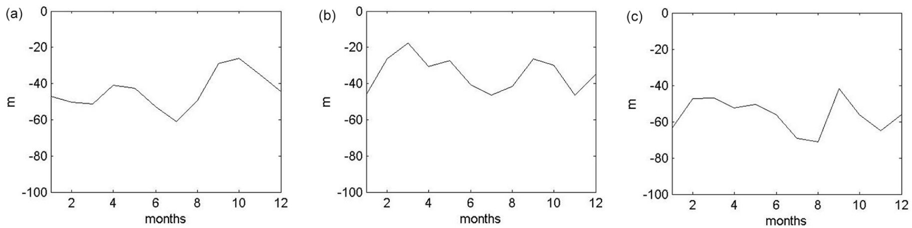

Figure 4. Seasonal pattern of the 15° isotherm depth **(a)**, the oxycline depth (44.6 µmol L^{-1}) **(b)** and the upper boundary of the OMZ depth (22.3 µmol L^{-1}) **(c)** during 1996–2009 time series.

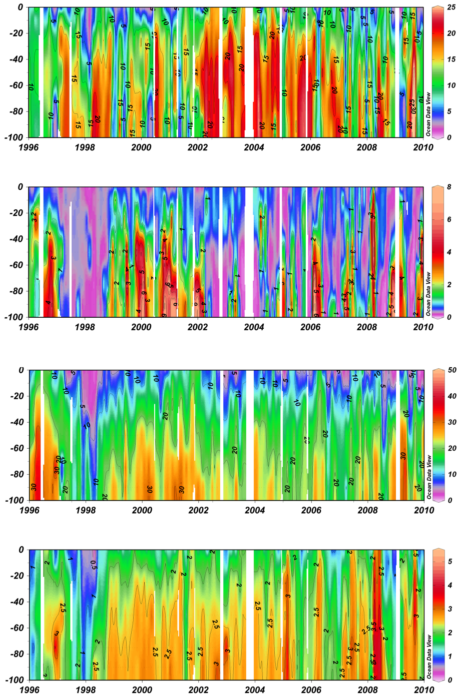

Figure 5. Temporal variability of water column nitrate (µM), nitrite (µM), silicate (µM) and phosphate (µM) distribution during the 1996–2009 time series. Solid and dashed contour line indicates the 22.3, 44.6 µmol L^{-1} oxy-lines.

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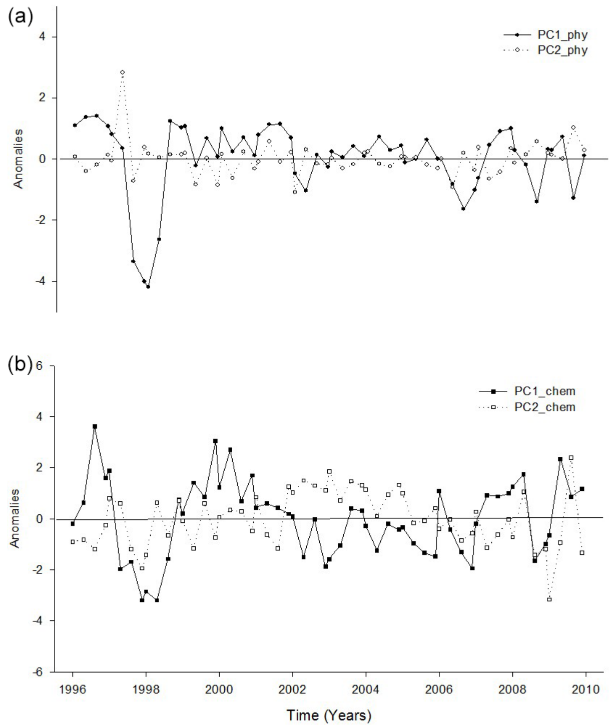

Figure 6. Temporal series of the first and second Principal Component (PC1, PC2) of the physical and chemical variables at St. 4 off Callao during 1996–2009.

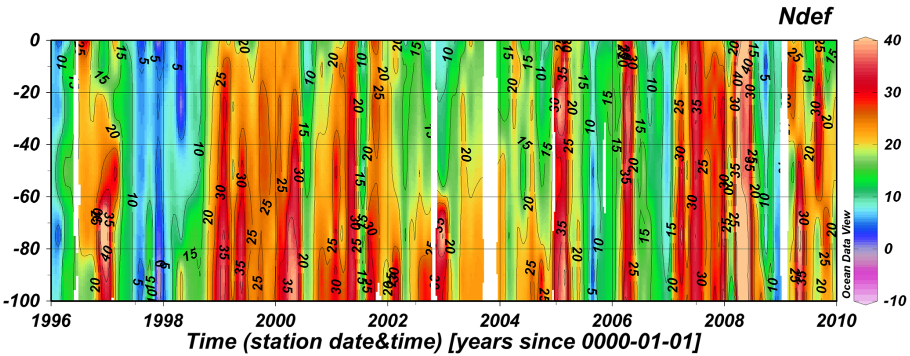

Figure 7. Temporal series of water column N deficit (Ndef = 12.6× [PO_4^{3-}] – ([NO_3^-]+[NO_2^-]) at St. 4 off Callao during 1996–2009.

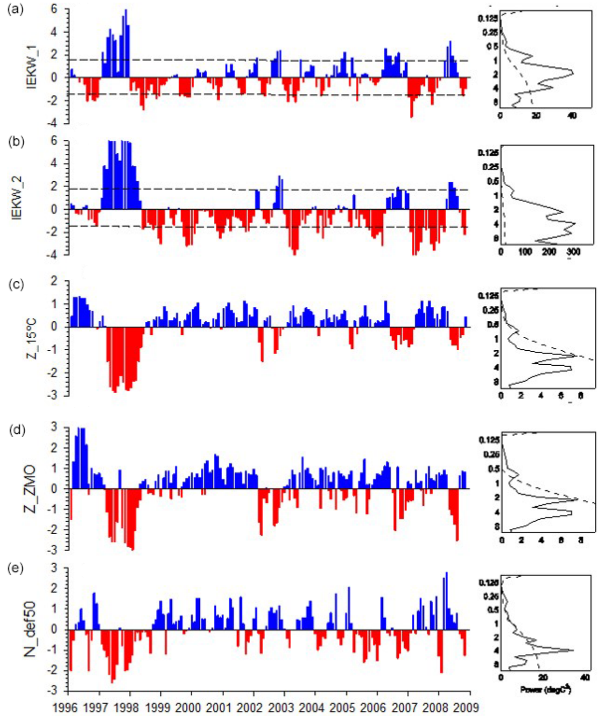

Figure 8. Temporal series of water column anomalies of the Intraseasonal Equatorial Kelvin Wave activity (IEKW) at 90° W for the first IEKW-1 and second baroclinic modes IEKW-2: **(a)**, **(b)** (The standard deviation over the study period is indicated by the horizontal dashed lines, time resolution of the data is every 5 days); depth of the thermocline **(c)**, OMZ's upper boundary depth **(d)** and N deficit at 50 m **(e)** at St. 4 off Callao during 1996–2008. On the left, different variables global spectrum wavelet analysis.

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