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Inter-decadal changes in the intensity of the Oxygen Minimum Zone off Concepción, Chile ($\sim 36^\circ$ S) over the last century

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Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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BGD

12, 6003–6035, 2015

**Inter-decadal
changes in the
intensity of the
Oxygen Minimum
Zone**

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

We reconstructed oxygenation changes in the Oxygen Minimum Zone of the upwelling ecosystem off Concepción (36° S), Chile, using inorganic and organic proxies in a sediment core covering the last ca. 110 years of sedimentation in this area. Authigenic enrichments of Mo, U and Cd were observed between ca. 1935–1971 CE indicating a prolonged period of more reduced conditions in bottom waters and surface sediments. Significant positive correlations ($p < 0.05$; Spearman) between redox sensitive metals, algal sterols, biomarkers of anaerobic microorganisms, and archaeal glycerol dialkyl glycerol tetraether indicated a coupling among bottom water oxygen depletion, and increased primary and export production, suggesting that the period with low O₂ of ca. 35 years, follows low frequency inter-decadal variation of the Pacific Decadal Oscillation, which may have resulted in O₂ depletion over the entire continental shelf off Concepción. Taken together with the concurrent increase in sedimentary molecular indicators of anaerobic microbes allow us to suggest that the prokaryote community has been influenced by changes in oxygenation of the water column.

1 Introduction

Oxygen Minimum Zones (OMZs) are epipelagic and mesopelagic subsurface layers of suboxic waters (e.g., $\leq 22 \mu\text{M O}_2$) found along eastern boundary currents such as the Eastern Tropical North and South Pacific, and the Benguela current, as well as the Arabian Sea and the Equatorial Pacific, where upwelling of nutrient-rich waters promotes elevated primary production and O₂ consumption through microbial respiration (Wyrtky, 1962; Helly and Levin, 2004; Paulmier and Ruiz-Pino, 2009). Due to the presence of strong redox gradients, reducing conditions and active microbial communities connecting the cycling of carbon, nitrogen, sulfur and other elements, OMZs are considered remnants of a past anoxic ocean due to their similarities with Archaeal prokaryotic biota (Ulloa et al., 2012; Wright et al., 2012).

BGD

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Waters overlaying the continental shelf of central Chile become seasonally depleted in O_2 during austral spring and summer when the area is fed by the poorly oxygenated Peru–Chile Countercurrent. In austral autumn and winter the shelf waters become oxygenated due to the input of Subantarctic waters (Ahumada and Chuecas, 1979; So-
 5 barzo et al., 2007). Inter-annual phenomena such as the El Niño Southern Oscillation (ENSO) can also impact oxygenation of south Pacific waters (Blanco et al., 2002; Carr et al., 2002; Levin et al., 2002). In central-southern Chile, the upper edge of the OMZ deepens during El Niño thus allowing greater oxygenation of bottom waters (Gutiérrez et al., 2000; Neira et al., 2001; Escribano et al., 2004). Analyzing a sedimentary record
 10 from northern Chile, Vargas et al. (2007) related changes in coastal upwelling and biological production with variations in the Pacific Decadal Oscillation (PDO), characterized by an ENSO-like interdecadal variability in the Humboldt Current System. During the cold phase of the PDO, primary production intensifies in response to upwelling and fertilization of the upper ocean (Mantua et al., 1997, 2002; Cloern et al., 2007), leading to enhanced oxygen consumption in the water column (Wyrtyk, 1962; Sarmiento et al.,
 15 1998; Helly and Levin, 2004). Since patterns of biological production and oxygenation of the water column during PDO cycles resemble those of ENSO (Vargas et al., 2007), we hypothesize that variations at the scale of the PDO promote chemical and biological changes in the OMZ off central-southern Chile.

Past redox variations can be analyzed using trace elements in sediments since redox sensitive metals are less soluble under reducing conditions resulting in authigenic enrichment in low oxygen and high organic matter environments (Algeo and Maynard,
 20 2004; McManus et al., 2005). This chemical behavior makes uranium (U), molybdenum (Mo), and cadmium (Cd) useful paleoredox and paleoproductivity proxies (Algeo and Maynard, 2004; McManus et al., 2005; Riquier et al., 2005).

In the past decade, an abundant and diverse microbial community has been detected in OMZ waters off central and northern Chile (Stevens and Ulloa, 2008; Farías et al.,
 25 2009; Quiñones et al., 2009; Canfield et al., 2010; Molina et al., 2010; Levipan et al., 2012; Srain et al., 2015). Temporal and compositional variations in this microbial com-

munity can be studied by analyzing their cell membrane lipids (biomarkers) preserved in the sedimentary record, as has been done for other OMZ areas of the world ocean (Schouten et al., 2000a; Arning et al., 2008; Rush et al., 2012).

We studied redox sensitive metals and organic biomarkers in a 110 year sedimentary record from the OMZ within the upwelling ecosystem off Concepción, central-southern Chile (36° S), to infer changes in biological production and oxygenation of the water column. Our goal was to assess whether the intensity of the OMZ has varied over the past century in response to ocean/atmosphere circulation patterns, and whether this has affected the prokaryote community.

2 Methods

2.1 Sampling

The study site (Station 18; 36°30.8' S 73°7' W) is located in the coastal upwelling ecosystem off central-south Chile at ca. 18 nautical miles from the coast of Concepción (Fig. 1). Sampling was carried out in the framework of the grant “Microbial Initiative in Low Oxygen off Concepción and Oregon” (http://mi_loco.coas.oregonstate.edu), and the Oceanographic Time Series Program (Station 18) of the Center for Oceanographic Research in the eastern South Pacific (COPAS) at University of Concepción (www.copas.udec.cl/eng/research/serie).

A 25 cm-long sediment core was collected at a depth of 88 m during austral summer (February 2009) using a GOMEX box corer onboard R/V *Kay-Kay II*. The top 5 cm were sectioned on board every 0.5 cm, whereas the rest of the core was sampled at 1 cm resolution. Samples were stored in glass petri plates and kept frozen at -18°C until laboratory analysis. Water column was sampled monthly at Station 18 from January 2008 to November 2009 with Niskin bottles, and values of temperature, salinity, oxygen, and fluorescence of chlorophyll *a* were obtained using a Seabird 25 CTDO.

BGD

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Fluorescence was transformed to chlorophyll *a* according to Parsons et al. (1984). All water column data were obtained from the database of the COPAS Center.

2.2 Sedimentary redox potential and organic carbon

Redox potential was measured in the top 15 cm of the sediment core using a redox potential sensor (Hanna) with an accuracy of ± 0.1 mV. Sedimentary organic carbon was determined by high temperature oxidation using a NA 1500 Carlo Erba elemental analyzer. Inorganic carbon was removed by putting the samples into an Ag cup and then fuming with concentrated HCl. After this, the samples were dried overnight at ca. 60°C and then wrap the Ag cup into a tin cup for analysis.

2.3 Geochronology

^{210}Pb activities were determined in sediment core sections by Alpha spectrometry of its daughter ^{210}Po using ^{209}Po as a yield tracer (Flynn, 1968). The activities were quantified until 1σ error was achieved in a Canberra Quad Alpha Spectrometer. The ages (CE, common era) were established according the constant rate of supply model (CRS, Appleby and Oldfield, 1978), which considers the unsupported ^{210}Pb inventories ($^{210}\text{Pb}_{\text{xs}}$). Geochronology of the sediment core was established through the best fit of curves of the ages obtained from the CRS model and three ^{14}C control points from longer cores retrieved in 2006 at the same sampling site (Muñoz et al., 2012, core VG06-2). Radiocarbon ages were converted to calendar years before present using calibration curve MARINE09 (Reimer et al., 2009) and applying a $\text{DR} = 137 \pm 164$ years and 2σ confidence interval (Table S1 in the Supplement).

2.4 Trace metal analysis

Trace metals molybdenum (Mo), uranium (U), and cadmium (Cd) were analyzed in an Agilent 7500ce Inductively Coupled Plasma-MS. Aluminum was determined in a Perkin Elmer Analyst 700 Atomic Absorption Spectrometer. Sediment samples

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



were prepared using sequential acid digestion (HNO_3 , HCl , HClO_4 , HF) until total dissolution. Analytical blanks were determined following the above procedure using $18.0\text{ M}\Omega$ water and subtracted from sample measurements. Accuracy and precision of measurements were assessed by the analysis of the National Research Council of Canada reference material MESS-3. Excess metal (Me_{xs}) was calculated as $[\text{Me}_{\text{sample}}] - ((\text{Me}/\text{Al})_{\text{earth}} \times [\text{Al}_{\text{sample}}])$. $(\text{Me}/\text{Al})_{\text{earth}}$ corresponds to an average ratio values for Biobío river (Fig. 1) in central-southern Chile (J. M. Muratli, personal communication, 2012).

2.5 Gas chromatography-mass spectrometry (GC-MS) of biomarkers

The extraction of lipids (i.e., hopanes, hopanols, sterols, and mono-*O*-alkyl-glycerol ethers – MAGEs) from sediments was carried out according to Bligh and Dyer (1959), substituting chloroform with dichloromethane. Freeze-dried sediment samples (1–5 g) were sequentially extracted by ultra-sonication with 30 mL dichloromethane/methanol (1 : 3 v/v, 2X), (1 : 1 v/v, 1X), and dichloromethane (2X). The lipid extract was concentrated with a rotary evaporator and dried with anhydrous Na_2SO_4 . Lipid extracts were then divided into four fractions by column chromatography using silica gel. Aliphatic hydrocarbons (F1) were eluted with 40 mL hexane, ketones (F2) were eluted with 50 mL toluene/hexane (1 : 3 v/v), alcohols (F3) eluted with 50 mL ethyl-acetate/hexane (1 : 9 v/v), and polar compounds (F4) eluted with 35 mL ethyl-acetate/methanol/hexane (4 : 4 : 1 v/v).

Samples were analyzed in an Agilent 6890 GC series coupled to an Agilent 5972 MS. The alcohol fraction (F3) was previously derivatized with 80 μL BSTFA (N,O-bis(trimethylsilyl) trifluoroacetamide) and 40 μL TMCS (trimethylchlorosilane) at 70°C for 1 h. Hopanols, sterols and MAGEs were analyzed with a 30 m DB-5 column (0.5 mm ID, 0.25 μm film thickness) using He as carrier gas. The GC oven temperature program was: 60°C (2 min) to 150°C at $15^\circ\text{C}\text{min}^{-1}$, to 320°C (held 34.5 min) at $4^\circ\text{C}\text{min}^{-1}$. Hopanes were analyzed in the aliphatic hydrocarbon fraction (F1) using a 30 m HP-5 column (0.32 mm ID, 0.25 μm film thickness). GC oven temperature program was:

80 °C (2 min) to 130 °C at 20 °C min⁻¹, to 310 °C at 4 °C min⁻¹. The MS was operated in electron impact mode (70 eV) with the ion source at 250 °C. Mass spectra were acquired in both full scan mode (*m/z* range 40–600, scan rate 2.6 s⁻¹) and selective ion-monitoring mode (SIM, *m/z* 191 for hopanes and hopanols). Concentrations of individual alcohols and aliphatic hydrocarbons were based on those of internal standards 1-nonadecanol and squalene, and were transformed to contents by normalization by organic carbon content.

2.6 Analysis of glycerol dialkyl glycerol tetraethers (GDGTs) by High Performance Liquid Chromatography – Atmospheric Pressure Chemical Ionization – Mass Spectrometry (HPLC-APCI-MS)

Sedimentary material was sequentially extracted by ultrasonication (3x) with methanol, dichloromethane-methanol (1 : 1, vol/vol), and dichloromethane. Lipid extracts were concentrated using a rotary evaporator and dried over a small Pasteur pipette filled with combusted glass wool and anhydrous Na₂SO₄. Lipids were separated into non-polar and polar fractions using a Pasteur pipette filled with activated Al₂O₃, after elution with hexane/dichloromethane (9 : 1, vol/vol) and dichloromethane/methanol (1 : 1 vol/vol), respectively. An aliquot of the polar fraction was dissolved in hexane/propanol (99 : 1 vol/vol) and filtered through a 0.45 μm PTFE filter. HPLC-MS analysis followed Hopmans et al. (2000) and Liu et al. (2012) using an Agilent Technologies 1200 Series HPLC equipped with an auto-sampler and a binary pump, linked to a Q-TOF 6520 mass spectrometer via an atmospheric pressure chemical ionization interface (Agilent Technologies). Samples were dissolved in 200 μL hexane/isopropanol (99 : 1 vol/vol). GDGTs were separated using a Prevail Cyano column (2.1 × 150 mm, 3 mm; Grace, USA) maintained at 35 °C and a flow rate of 0.25 mL/min. The elution program was: 5 min 100 % eluent A (hexane/isopropanol, 99 : 1, vol/vol), followed by a linear gradient to 100 % eluent B (hexane/isopropanol, 90 : 10 vol/vol) in 35 min, and then held at

BGD

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

100% eluent B for 5 min. Quantification of core GDGTs was achieved by co-injection of samples with a C₄₆GDGT as internal standard (Huguet et al., 2006).

2.7 Statistical analysis

5 Homogeneity of variances was assessed using the Levene's test, whereas normality was determined using a Shapiro–Wilk test. Non-parametric Spearman correlations were calculated between selected variables in order to determine statistical associations with significance < 0.05 (Software Statistica, version 12).

3 Results

3.1 Oceanographic setting of the study site

10 During austral fall and winter (April to August), temperature ranged between 11 and 12 °C in the upper 20 m of the water column, and between 10 and 11 °C below 65 m depth (Fig. 2a). Surface salinity varied between 32 and 33 above 20 m, and was 34 below this depth (Fig. 2b). Chlorophyll *a* concentration varied between 0.3 and 1.4 mg m⁻³ with higher values in the top 20 m (Fig. 2c). Oxygen concentration varied between 170 and 205 μM in the top 20 m, and lower than 22 μM (suboxia) below 60 m depth (Fig. 2d).

15 During austral spring and summer (September to March) surface temperature ranged between 13 and 15 °C, decreasing to 10 °C below 84 m depth (Fig. 2a). Salinity varied between 31 and 34.5 in the whole water column (Fig. 2b). Chlorophyll *a* concentrations up to 53 mg m⁻³ were measured in surface waters (Fig. 2c). Oxygen concentration ranged between 114 and 217 μM in surface waters. Suboxic waters (i.e.,
20 < 22 μM) occur below ca. 20 m (Fig. 2d), which is significantly shallower than in austral fall-winter when dissolved O₂ values lower than 22 μM below ca. 60 m depth.

BGD

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3.2 Sedimentary redox potential and organic carbon

Redox potential decreased from -176 mV at the water–sediment interface to -325 mV below 3 cm, indicating predominance of reducing conditions in near-surface sediments at the time of sampling during austral summer (Fig. 2e), consistent with the occurrence of $5 \mu\text{M O}_2$ in bottom waters of (Fig. 2d). A surface fluffy layer with a *Thioploca* mat was observed at the sediment–water interface. Organic carbon content varied between 2 to 4 wt.% (Fig. 2e).

3.3 Geochronology

$^{210}\text{Pb}_{\text{xs}}$ activity was detected down to 23 cm in the core where reached background values of 0.80 ± 0.02 dpm g^{-1} . The geochronology was estimated using CE ages from $^{210}\text{Pb}_{\text{xs}}$ inventories (Table S1) transformed to Cal BP years and calibrated ages from radiocarbon measurements values fitted a polynomial curve (r^2 0.99) allowing to adjust ages at the bottom of the core, that generates errors with the CRS model (Binford, 1990). A recent sedimentation rate of 0.24 ± 0.02 cm yr^{-1} was established and an exponential decreased is observed due to sediment compaction (Fig. 2f). Thus, the core represents ca. 110 years of sedimentation at Site 18.

3.4 Redox sensitive trace metals

Redox sensitive metals are most enriched in the interval ca. 1935–1970 CE (Fig. 3a–c; black bar). Excess molybdenum (Mo_{xs}) content ranged between 2.5 and 6.5 ppm (Fig. 3a), showing a similar vertical distribution as uranium (U_{xs}) that ranged between 1.1 to 4.1 ppm (Fig. 3b), and Cd_{xs} , which ranged between 1.9 and 0.8 ppm (Fig. 3c). Enrichments of Mo_{xs} , U_{xs} , and Cd_{xs} exhibited a significant correlation among each other (R_s : 0.6; $p < 0.05$) indicating lower O_2 depletion conditions in the bottom waters and sediments at this time. In comparison, the periods 1905–1919 CE and 1979–2005 CE

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

showed lower contents of redox-sensitive metals (Fig. 3a–c; white bars), and presumably more oxygenated bottom waters and sediments.

3.5 Algal sterols

Sterols C27^{Δ5}, C28^{Δ5}, C29^{Δ5} and C30^{Δ22} were identified through the fragmentation pattern of their trimethylsilyl (TMS) derivatives. The presence of C27^{Δ5}-sterol (m/z 458 [M]⁺) was confirmed due to the detection of fragments m/z 129, m/z 329 and 368. C28^{Δ5}-sterol (m/z 472 [M]⁺) showed a base peak fragment at m/z 129, as well as m/z 343 and m/z 382. C29^{Δ5}-sterol (m/z 486 [M]⁺) was identified by prominent m/z fragments at 357 and 396. Prominent fragments m/z 69, m/z 271, m/z 359 and m/z 500 [M]⁺ confirmed the presence of C30^{Δ22} dinosterol. The sterol content ranged between 1029 and 12 164 $\mu\text{g}(\text{gC}_{\text{org}})^{-1}$ with maximum values in surface sediments (Fig. 4a). Sterols correlated positively with U_{xs} (R_s : 0.4, $p < 0.05$).

3.6 Archaeal GDGTs

GDGTs were identified by their molecular ion and elution pattern: GDGT-0 (1302 [M + H]⁺), GDGT-I (1300 [M + H]⁺), GDGT-II (1298 [M + H]⁺), GDGT-III (1296 [M + H]⁺), and GDGT-V and GDGT-V' (1292 [M + H]⁺ known as crenarchaeol and crenarchaeol regioisomer). The concentration of GDGTs varied between 1094 and 5423 $\mu\text{g}(\text{gC}_{\text{org}})^{-1}$ (Fig. 4b), with elevated values at the base core and between ca. 1947 and 1975 CE (Fig. 4b). A positive correlation was found between GDGTs concentration and U_{xs} content (R_s : 0.6; $p < 0.05$).

3.7 Geohopanoid composition and abundance

C₂₇-trisorhopene (22,29,30 trisorhop-17,(21)-ene) was identified based on its molecular ion fragment m/z 368 [M⁺-2H⁺] and fragments m/z 191 and 231 indicating unsaturation at the ring system (Table 1). Three diploptene isomers were identified according

BGD

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

with their mass spectra, hop-13,18-ene, neohopene, and hop-22,29-ene (Fig. 5a, Table 1). The C₃₀ hopene diploptene was identified based on its molecular ion (m/z 410 [M⁺]) and diagnostic ions m/z 395, 299 and 191 (Fig. 5a, Table 1). A homologous series of C₃₁ to C₃₅ hopanes with the $\alpha\beta$ configuration were identified through m/z 191 in the hydrocarbon fraction (Fig. 5a). Homohopanes C₃₁, C₃₃, C₃₄, and C₃₅ were present as epimers S and R (Fig. 5a, Table 1), whereas C₃₂ hopane occurred as epimer R (Fig. 5a; Table 1). C₂₇ norhopene, and hopanes C₃₀ and C₃₁ were the only compounds with $\beta\beta$ configuration (Fig. 5a, Table 1). C₃₁ hopane showed the highest relative abundance in the homohopane homologous series, with S and R 17 α ,21 β homohopane as predominant compound, followed by C₃₃ and C₃₄ (Fig. 5a).

17 β ,21 β hopanol (C₃₀), 17 β ,21 β homohopanol (C₃₁), 17 β ,21 β bishomohopanol (C₃₂), and 17 β ,21 β trishomohopanol (C₃₃) were identified detecting m/z 191 and their molecular ions ([M]⁺ m/z 500, m/z 514, m/z 528, and m/z 542) (Fig. 5b, Table 1). The most abundant hopanol was homologue C₃₂ (Fig. 5b).

C₂₇-trisorhopene ranged between 0.03 and 1.1 $\mu\text{g}(\text{gC}_{\text{org}})^{-1}$. Maximum values occurred between ca. 1935 and 1970 CE (Fig. 4c), whereas minimum values were observed during periods 1905–1928 CE and 1980–2005 CE (Fig. 4c). C₂₇-trisorhopene correlated positively with U_{xs} and Cd_{xs} (R_s : 0.5; $p < 0.05$). Content profile of C₃₁ hopanol varied between 1.1 and 3.7 $\mu\text{g}(\text{gC}_{\text{org}})^{-1}$, and reached the highest value during period 1935–1970 CE (Fig. 4d). Positive correlations between C₃₁ hopanol, Mo_{xs}, and Cd_{xs} were observed (R_s : 0.6 and 0.4 respectively; $p < 0.05$). In contrast, C₃₂ hopanol anticorrelated with C₃₁ hopanol and U_{xs} (R_s : -0.5, $p < 0.05$; Fig. 4e).

3.8 Mono-O-alkyl glycerol ethers (MAGEs) indicators of fermentative and sulfate reducing bacteria

Mass spectra of MAGEs showed a base peak fragment of m/z 205 characteristics of monoalkyl glycerol-TMS compounds, which corresponds to cleavage between carbons 1 and 2 of the glycerol moiety, and fragment m/z 445 [M + H-CH₃]⁺ that corresponds

BDG

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

to a loss of methyl group. We identified C₁₆-MAGE with molecular ion m/z 460 [M]⁺, C₁₇-MAGE with m/z 474 [M]⁺, and C₁₈-MAGE with m/z 488 [M]⁺.

The content of MAGEs (sum of C₁₆, C₁₇, and C₁₈ MAGEs) varied between 9 and 628 μg(gC_{org})⁻¹ (Fig. 4f). MAGEs content remained low during the period 1901–1928 CE with an average concentration of 50 μg(gC_{org})⁻¹ (Fig. 4f). From ca. 1935 CE, MAGEs concentrations increased reaching the highest content in surface sediments (Fig. 4f). MAGEs correlated positively with Mo_{xs} (R_S: 0.4, $p < 0.05$) and Cd_{xs} (R_S: 0.6, $p < 0.05$).

4 Discussion

4.1 Patterns of redox depositional conditions, primary and exported production

We interpret variations in contents of sedimentary redox sensitive metals as changes in oxygenation of bottom waters and surface sediments. This interpretation is coincident with previous observations by Muñoz et al. (2012) for the same sampling site, and authigenic enrichments of Mo over the Oregon shelf associated with O₂ depletion and increased primary productivity (Erhardt et al., 2014). U and Mo authigenic enrichment occur under O₂-depleted conditions (Eriksson and Helz, 2000; Siebert et al., 2003; Algeo and Tribovillard, 2009). Cd is an element that becomes enriched in sediments in the presence of pore water sulfide as export production increases (Tribovillard et al., 2004, 2006). We interpret Cd enrichment in sediments as indicative of higher export production from the water column.

Variations in the abundance of total algal sterols (sum of C27^{Δ5}, C28^{Δ5}, C29^{Δ5} and C30^{Δ22}) are considered to represent changes in primary and export production to the sediment. Changes in the abundance of isoprenoidal GDGTs are used as an indication of variations in ammonia oxidation by marine pelagic archaea (De Long et al., 1998; Schouten et al., 2000b; Turich et al., 2007; Lincoln et al., 2014). The preservation of

BGD

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



C₂₇-trisnorhopene is favored in anoxic and euxinic environments, and during upwelling events (Grantham et al., 1980; Schouten et al., 2001), and is considered an indicator of anaerobic microbial degradation (Volkman et al., 1983; Duan et al., 1996; Duan, 2000; Peters et al., 2005).

Fluctuations in bacterial hopanes and hopanols are related to variations in bacterial groups (Ourisson and Albrecht, 1992; Innes et al., 1998; Rohmer et al., 1984; Talbot et al., 2007). MAGEs C₁₆, C₁₇, and C₁₈ mono-*O*-alkyl glycerol ethers are present in fermentative and sulfate reducing bacteria (Langworthy et al., 1983; Langworthy and Pond, 1986; Ollivier et al., 1991), although this biological source does not appear to be unique (Hernández-Sanches et al., 2014). That said, the statistical relationship found between MAGEs ($R_s < 0.05$) and reducing conditions in the core collected from 18 St. is explained as changes in abundance and occurrence of bacteria involved in microareophilic and anaerobic metabolism, in response to variations in water column oxygenation over the continental shelf off Concepción.

The downcore distribution of inorganic and organic proxies reveal a period of ca. 35 years between ca. 1935 and 1970 CE (Figs. 3 and 4; black bar) when redox sensitive metals (Fig. 3), sterols (Fig. 4a), GDGTs (Fig. 4b), C₂₇ trisnorhopene (Fig. 4c), C₃₁ hopanol (Fig. 4d), and MAGEs (Fig. 4f) were higher. Taken together, these patterns allow us to infer that water column O₂ was comparatively lower than during those periods immediately above and below, in association with enhanced primary production reflected in increase of sterols and GDGTs contents (Fig. 4a). Likewise, two periods with relatively more ventilated and oxygenated conditions are evident between ca. 1901 and 1919 CE, and between ca. 1979 and 2005 CE (Figs. 4 and 5). Both of these periods were characterized by low metal enrichments (Fig. 3), a lower content of bacterial biomarkers related to oxygen depleted conditions such as C₂₇ trisnorhopene, C₃₁ hopanol, and MAGEs (Fig. 4c, d and f), and lower organic matter fluxes evidenced by low contents of sedimentary sterols (Fig. 4a) and GDGTs (Fig. 4b).

We suggest that from ca. 1935–1970 CE there was higher export production, and that this export is responsible for the increase in phytoplankton sterols (Fig. 4a), con-

BGD

12, 6003–6035, 2015

**Inter-decadal
changes in the
intensity of the
Oxygen Minimum
Zone**

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

current with an increase in Cd (Fig. 3) and GDGTs (Fig. 4b). An enhanced sinking of organic matter leads to a subsequent increase in O₂ consumption by microbial degradation, potentially depleting O₂ in the water column (Helly and Levin, 2004; Canfield, 2006) and sediments. Such conditions lead to Mo, U and Cd enrichment sediments. Higher GDGTs content during this same time period (Fig. 4b) may reflect better preservation favored by severe O₂ depletion. The positive correlation between sterols, GDGTs, and U enrichments support this conclusion, since U enrichment occurs under low O₂ concentration and/or high organic matter deposition (Dezileau et al., 2002; Tribouillard et al., 2006; Muñoz et al., 2012). Schouten et al. (2004) and Zonneveld et al. (2010) reported that GDGTs preservation is lower in oxygenated than in suboxic-anoxic settings.

4.2 Changes in microbial communities in response to redox variation

Hopanols C₃₁ and C₃₂ are used to analyze changes in the bacterial community structure because they are the diagenetic products of bacteriohopanetetrols (BHPs), which in turn can have different bacterial sources (Talbot et al., 2003). The hopanol content was dominated by C₃₂ hopanol whose predominance in recent sediments has been previously reported (Buchholz et al., 1993; Innes et al., 1997, 1998; Talbot et al., 2003).

An increase in C₃₁ hopanol content between ca. 1935 and 1970 CE (Fig. 4d) is indicative of low oxygen if analyzed in light of the positive correlation between Mo_{xs} and Cd_{xs} (R_s: 0.6 and 0.4 respectively; $p < 0.05$). The content of C₃₂ hopanol, a diagenetic product of BHTs (Innes et al., 1998; Talbot et al., 2003), mostly produced by heterotrophic aerobic bacteria (Rohmer et al., 1984), exhibited a slight decrease (Fig. 4e) concurrent with the enrichment of C₃₁ hopanol (Fig. 4d) and redox sensitive metals (Fig. 3). Observed changes in abundance and distribution of C₃₁ and C₃₂ hopanols in concomitance with past variations of oxygen in the water column at the study site are consistent with previous findings by Saenz et al. (2011) and Kharbush et al. (2013). These authors found that the abundance and structural diversity of BHPs, the biological sources of hopanoids, increase with decreasing oxygen in the water column of

the Peruvian margin, Arabian Sea, Cariaco Basin, and in the Eastern Tropical North Pacific.

Trisnorhopanes are bacterial lipid markers associated with upwelling and anoxic depositional environments, although its biological source has not yet been identified (Schouten et al., 2001; Peters et al., 2005). The highest C₂₇ trisnorhopene (Fig. 4c) contents occurred during the period of high primary production and O₂ depletion, suggesting a relationship between its abundance and upwelling-favorable conditions and anaerobic bacterial activity, as previously suggested (Grantham et al., 1980; Duan et al., 1996; Duan, 2000; Schouten et al., 2001).

The sedimentary content of MAGEs was also higher in the period 1935–1970 CE and in the topmost sediments (Fig. 4f). MAGEs have been detected in sediments from upwelling regions of Namibia, Peru, and central-southern Chile and are attributed to the occurrence of sedimentary sulfate reducing bacteria (Arning et al., 2008). The presence of sulfate reducing bacteria has been previously documented as well for coastal waters of Chile (Canfield et al., 2010) and Peru (Finster and Kjeldsen, 2010).

4.3 Forcing of variations in the intensity of OMZ in central-southern Chile

The combined records of redox-sensitive metals and biomarkers suggest the occurrence of enhanced reducing conditions, both in the water column and at the sediment–water interface, from ca. 1935 until 1970 CE (Figs. 3 and 4), that roughly coincide with a cool (negative) phase of the Pacific Decadal Oscillation (PDO) (Fig. 4g). This suggests a link between changes in continental shelf oxygenation off Concepción and the PDO cycle, with alternating phases of decreased (1901–1930 and 1979–1997 CE) and enhanced upwelling (ca. 1935 to 1970 CE). The PDO is a recurring pattern of ocean–atmosphere variability in which the Pacific central gyre cools down while the eastern margin warms up, with phases that last between two and three decades (Mantua et al., 1997, 2002). The PDO plays a major role in decadal-scale oceanographic variability in the Pacific Ocean (Mantua et al., 1997, 2002; White and Cayan, 1998; Johnson and McPhaden, 1999). During cool or negative phase, the western Pacific becomes

BGD

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



warmer while parts of the eastern Pacific become colder. The reverse pattern occurs during warm or positive phase.

Periods of favorable upwelling conditions off central Chile may have been triggered by an enhanced thermal contrast between the sea-surface and land during negative phases of the PDO (Bakun, 1990; Vargas et al., 2007). Negative correlations between PDO index values with algal sterols (Figs. 4a and g; R_s : -0.3 ; $p < 0.05$) and GDGTs (Figs. 4b and 5g; R_s : -0.2 , $p < 0.05$) suggest an inverse relationship between the PDO and primary and export production at the study site, at least during the last 110 years. Interdecadal variations of enhanced coastal-upwelling conditions, recorded in sediments obtained from Mejillones Bay (23° S) during the last century, have been previously reported by Vargas et al. (2007). These authors suggested that decreased anomalous sea surface temperatures during interdecadal ENSO-like conditions might have exacerbated the land–sea thermal contrast, which in turn intensified the wind stress responsible of upwelling events.

Negative correlations between sedimentary C_{27} -trisanthracene, C_{31} hopanol, MAGEs, and PDO values ($R_s = -0.3, -0.4, 0.3, -0.2$, respectively; $p < 0.05$) and a positive correlation between C_{32} hopanol ($R_s = 0.3$) and PDO suggest that this wide-basin climatic anomaly has an impact on local oceanographic conditions off Concepción that in turn modulate the structure of the prokaryotic community. Bacterial C_{31} hopanol and MAGEs derive from microorganisms associated with marked chemoclines and redox gradients (Rohmer et al., 1984; Innes et al., 1997, 1998; Talbot et al., 2003, 2007) showed an inverse correlation with PDO index ($R_s: -0.4$ with C_{31} hopanol, -0.3 with MAGEs, $p < 0.05$). Thus, positive PDO phases (warm) were likely associated with a decrease in wind-driven upwelling, greater oxygenation, decreased primary productivity, and a concomitant decrease of microorganisms associated with low oxygen. Reverse conditions must have dominated during negative PDO phases, with more upwelling and primary production.

Previous studies in the Pacific Basin have evidenced connections between the PDO and variations in marine ecosystems, including perturbations in commercially impor-

BGD

12, 6003–6035, 2015

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

tant fish populations, salmon catches and stocks, and recruitments of ground-fish stocks (Kawasaki, 1991; Adkinson et al., 1996; Yasuda et al., 1997; Hollowed et al., 1998; Peterman et al., 1998). Deutsch et al. (2011) reported that decadal climate oscillations could cause nutrient depletion for photosynthesis due to enhanced nitrogen removal in the marine water column during the positive phase of PDO (warmer surface water). Here, we show the effects of the PDO on the structure of the planktonic prokaryotic community based on bacterial and archaeal biomarkers. Significant negative correlations were detected between the PDO and C_{31} hopanol ($R_s = -0.4$, $p < 0.05$), and GDGTs ($R_s = -0.2$, $p < 0.05$). Microaerophilic methanotrophic bacteria that flourish under high methane and low oxygen environments (Hanson and Hanson, 1996) could be a biological precursor of the observed C_{31} hopanol in the sedimentary record (Rohmer et al., 1984; Talbot et al., 2001). Higher content of sedimentary C_{31} hopanol during the cold (negative) phase of PDO from ca. 1930–1970 (Fig. 4d and g) could be the result low oxygen concentrations in the water column that could have favored the presence of methanotrophic bacteria along the oxycline, where comparatively high methane and low oxygen concentrations prevail (Scranton and Brewer, 1977; Farías et al., 2009), and where micro-aerophilic methane oxidation occurs (Blumenberg et al., 2007; Farías et al., 2009; Berndmeyer et al., 2013). At Station 18, Farías et al. (2009) found that dark chemoautotrophy related to aerobic oxidation of methane occurs in the oxycline mainly during active upwelling. In addition, the relatively higher content of GDGTs during the negative phase of the PDO (Fig. 5b and g) could be indicative of enhanced outgassing of N_2O to the atmosphere, since marine ammonia oxidizing archaea have been suggested as responsible for a great proportion of oceanic N_2O production (Santoro et al., 2011).

5 Conclusions

Our main goal was to assess the use of redox sensitive metals and organic biomarkers in the sedimentary record on the shelf off Concepción, Chile (36° S) as proxies for

changes in the intensity of the Oxygen Minimum Zone over the past century, and how these changes may have affected the microbial planktonic community. Our conclusions are summarized as follows:

1. Sedimentary sensitive redox metals and organic biomarkers indicate interdecadal variations in the intensity (oxygenation) of the Oxygen Minimum Zone during the last 110 years.
2. Inorganic and organic sedimentary proxies reveal that enhanced O₂-depleted conditions dominated from ca. 1935 to 1970 CE and were synchronously with more favorable upwelling conditions.
3. We suggest that variations in the Pacific Decadal Oscillation could be the physical mechanism controlling interdecadal variations of redox conditions in the coastal upwelling ecosystem off Concepción, influencing the composition of the microbial community, and that negative phases of the PDO correlate with decreased oxygenation on the inner continental shelf off Concepción

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Author contributions. The study was initiated and designed by B. Srain and S. Pantoja. B. Srain carried out field work and sample preparation. B. Srain, J. Sepúlveda, and J. McKay performed chemical analysis, and P. Muñoz and M. Salamanca did geochronology. All data analysis, including statistical analysis, was done by B. Srain advised by S. Pantoja, C. B. Lange, J. Sepúlveda and R. E. Summons. All authors contributed to data interpretation and general discussion. B. Srain wrote the manuscript with major inputs from S. Pantoja, J. Sepúlveda and C. B. Lange.

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Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

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Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

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Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

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Table 1. Compounds identified in the m/z 191 mass chromatogram of aliphatic hydrocarbon and alcohol fractions from shelf sediments off Concepción (36° S).

Symbol	Component	Number of carbon atoms	Molecular weight
Hopananes			
1	17a-22,29,30-trinorhopane	27	370
2	22,29,30-trinor-hop-17(21)-ene	27	368
3	17 β -22,29,30-trinorhopane	27	370
4	17a,21a-30-norhopane	29	398
5	17 β ,21 β -norhopene	27	368
6	17 β ,21 β -hopane	30	412
7	Neohop-13(18)-ene	30	410
8	17a,21 β -hopene	30	410
9	Hop-22(29)-ene	30	410
10	17a,21 β -homohopane (R)	31	426
11	Diploptene	30	410
12	17a,21 β -bishomohopane (R)	32	440
13	17 β ,21 β -homohopane	31	426
14 _{S/R}	17a,21 β -trishomohopane (S-R)	33	454
15 _{S/R}	17a,21 β -tetrahomohopane (S-R)	34	468
16 _{S/R}	17a,21 β -pentakishomohopane (S-R)	35	482
Hopanols			
17	17 β ,21 β -hopanol	30	500
18	17 β ,21 β -homohopanol	31	514
19	17 β ,21 β -bishomohopanol	32	528
20	17 β ,21 β -trishomohopanol	33	542

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

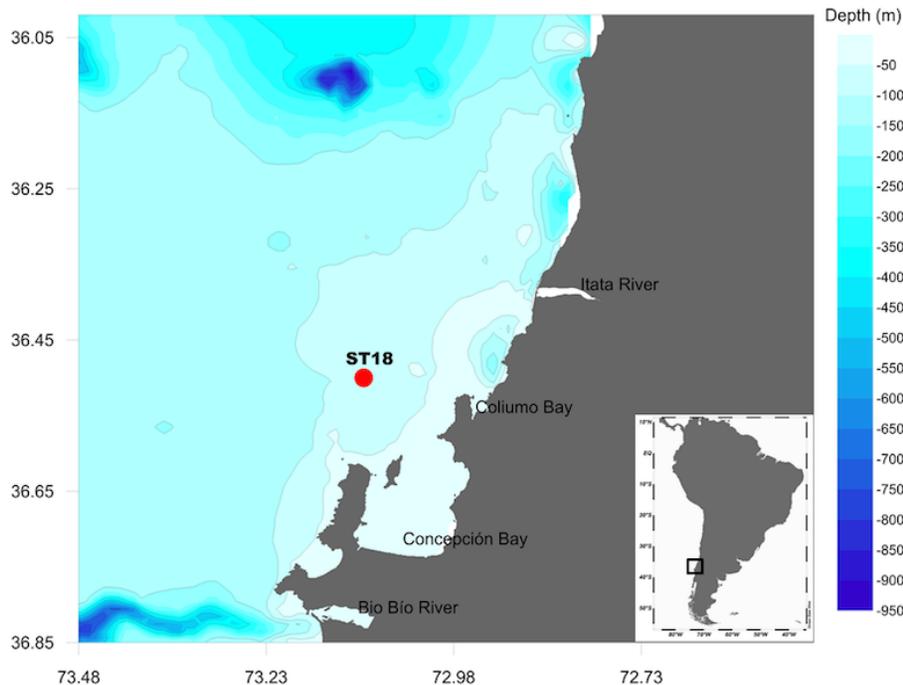


Figure 1. Location of sampling site Station 18 in the upwelling ecosystem off Concepción, central-southern Chile. Bathymetry in shades of blue, scale on right-hand side.

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

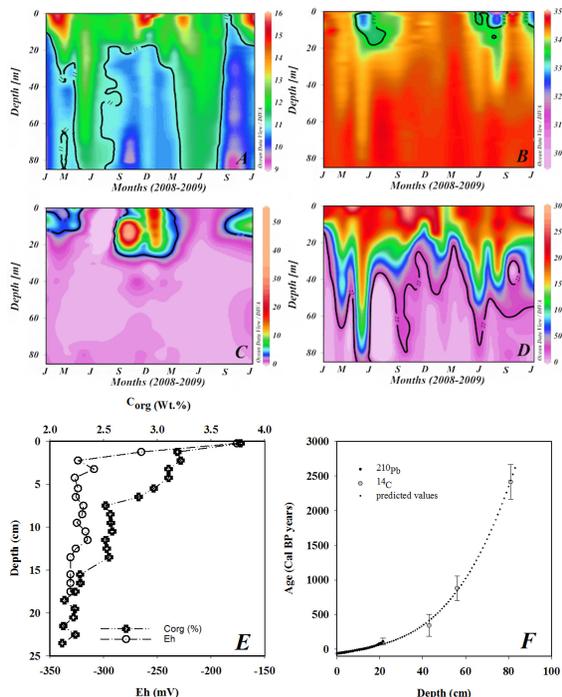


Figure 2. Oceanographic variability in the water column off Concepción (36° S) from January 2008 to January 2009: **(a)** temperature (°C); **(b)** salinity (psu); **(c)** chlorophyll (mg m⁻³); **(d)** dissolved O₂ (μM); and **(e)** redox potential (Eh) and organic carbon content (Wt.%) in the sediment core recovered from Station 18 in February 2009 (austral summer). Data collected by the Center for Oceanographic Research in the eastern South Pacific at the Oceanographic Time Series Station 18 (www.copas.udec.cl/eng/research/serie/). Data for **(e)** was provided by R. Quiñones. **(f)** Geochronology estimated from ²¹⁰Pb_{xs} inventories (black line) and ¹⁴C measurements ± standard deviation. All ages are expressed as years before present (1950). Dotted line shows the predicted values from the curve ($r^2 = 0.99$).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

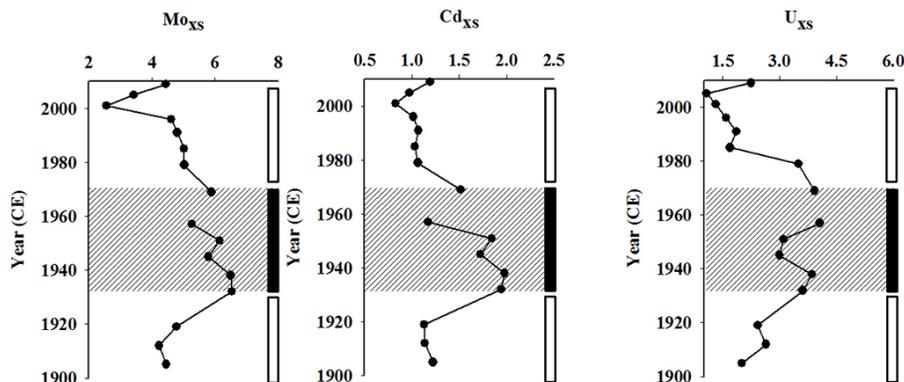


Figure 3. Downcore excess content of redox sensitive metals **(a)** Mo, **(b)** U, and **(c)** Cd. Shaded area and black bars corresponds to a period of ca. 35 years of enhanced authigenic precipitation of redox sensitive metals compared to periods of higher oxygenation (white bars) and low authigenic precipitation. CE = Common Era.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

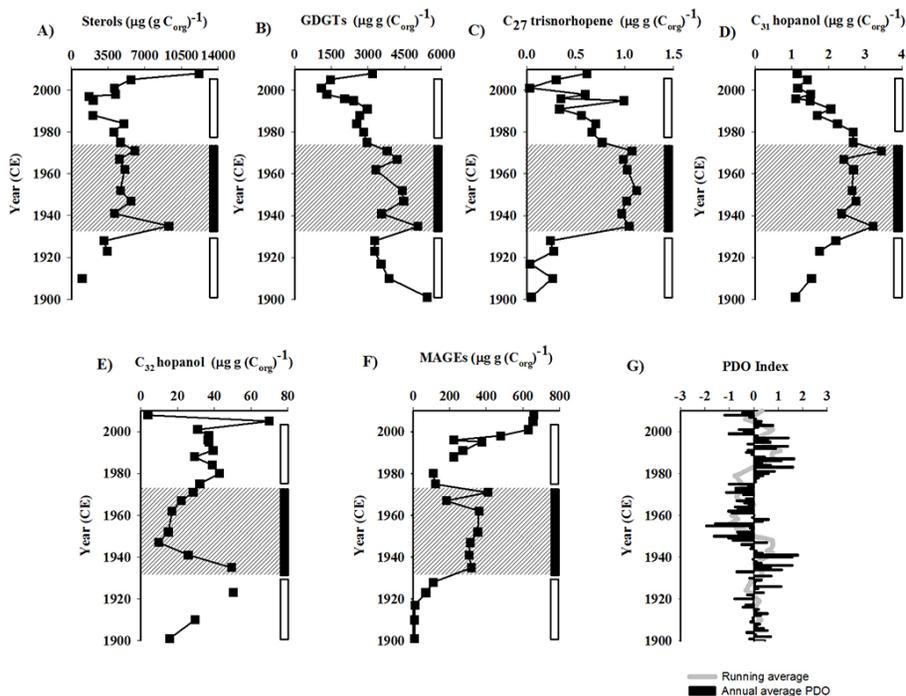


Figure 4. Downcore content of **(a)** sterols, **(b)** archaeal GDGTs, **(c)** C_{27} -TNH, geo-hopanoid, **(d)** C_{31} hopanol, **(e)** geo-hopanoid C_{32} hopanol, **(f)** MAGEs, and **(g)** Pacific Decadal Oscillation index (<http://jisao.washington.edu/pdo/PDO.latest>). Units are micrograms per gram organic carbon. Shaded area and vertical bars, and chronology as in Fig. 3.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Inter-decadal changes in the intensity of the Oxygen Minimum Zone

B. Srain et al.

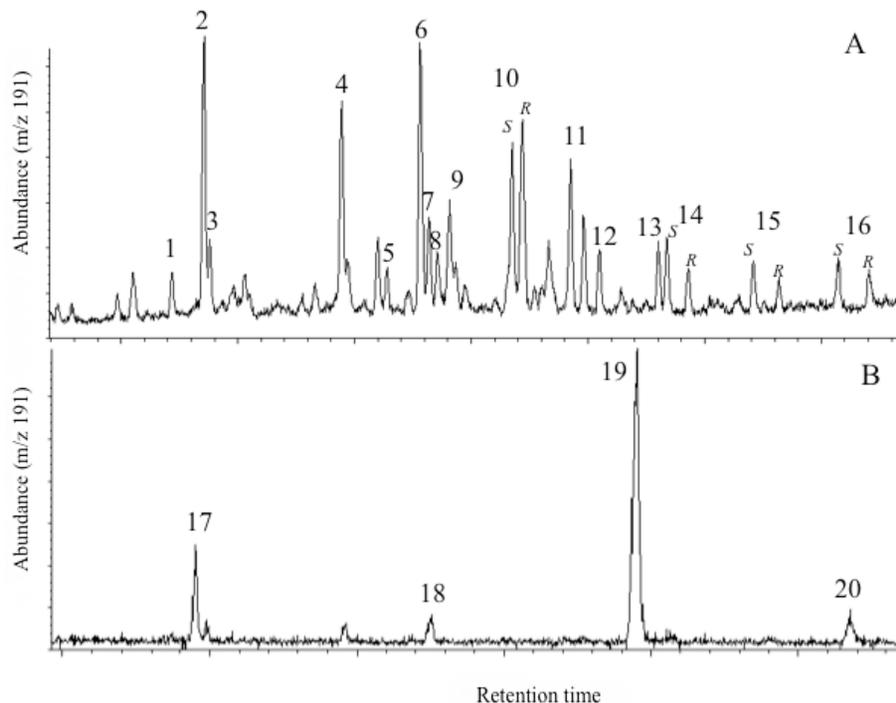


Figure 5. Representative GC-MS chromatograms of m/z 191 of (a) aliphatic hydrocarbons, and (b) TMS-derivatized alcohols from shelf sediments off Concepción (36° S). Numbers identify molecules as listed in Table 1, and S, R are epimers of the hopane series.