

Isotopic Characterization of Water Masses in the Southeast Pacific Region: Paleoceanographic Implications



Key Points:

- The first biogeochemical and spatial characterization of $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ from coastal water masses in the Southeast Pacific (SEP)
- The upper 1,000 m between the open ocean and coastal regions show strong differences in water mass chemistry and geometry
- Coastal data provide information that can aid in reconstructions of past ocean conditions in the SEP

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract In this study, we used stable isotopes of oxygen ($\delta^{18}\text{O}$), deuterium (δD), and dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) in combination with temperature, salinity, oxygen, and nutrient concentrations to characterize the coastal (71° – 78°W) and an oceanic (82° – 98°W) water masses (SAAW—Subantarctic Surface Water; STW—Subtropical Water; ESSW—Equatorial Subsurface water; AAIW—Antarctic Intermediate Water; PDW—Pacific Deep Water) of the Southeast Pacific (SEP). The results show that $\delta^{18}\text{O}$ and δD can be used to differentiate between SAAW-STW, SAAW-ESSW, and ESSW-AAIW. $\delta^{13}\text{C}_{\text{DIC}}$ signatures can be used to differentiate between STW-ESSW (oceanic section), SAAW-ESSW, ESSW-AAIW, and AAIW-PDW. Compared with the oceanic section, our new coastal section highlights differences in both the chemistry and geometry of water masses above 1,000 m. Previous paleoceanographic studies using marine sediments from the SEP continental margin used the present-day hydrological oceanic transect to compare against, as the coastal section was not sufficiently characterized. We suggest that our new results of the coastal section should be used for past characterizations of the SEP water masses that are usually based on continental margin sediment samples.

Plain Language Summary The Southeast Pacific (SEP) is a large marine region along the western continental margin of South America, where water masses that are transported from equatorial, subtropical, and subpolar latitudes converge. This study aims to understand the characteristics of water masses using isotopes of oxygen ($\delta^{18}\text{O}$), deuterium (δD), and dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) along with other parameters, such as temperature, salinity and oxygen, and nutrient concentrations. Significant differences in the chemical and isotope composition of SEP water masses are described. The distribution of the water masses above 1,000 m differs between our new coastal (71° – 78°W) and partly existing oceanic (82° – 98°W) sections. This

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has implications for the interpretation of paleoceanographic records, which are typically collected from the continental margin rather close to the coast.

1. Introduction

The coastal region of the Southeast Pacific (SEP) off Peru and Chile (as far as 38°S; Figure 1) hosts one of the most productive Eastern Boundary Current Upwelling Systems of the world (Chavez & Messié, 2009; Daneri et al., 2000; Montero et al., 2007). It has a complex water mass structure with a confluence of surface, subsurface and intermediate water masses coming from the subantarctic and the tropical Pacific, and recirculated deep waters (e.g., Silva et al., 2009; Strub et al., 1998). The interplay of these different waters plays a crucial role in the distribution of nutrients, heat, gases, and salt, which influence primary productivity, ocean circulation, and climate. Physical and chemical variables, such as temperature, salinity, and nutrients have been traditionally used to characterize water masses in the SEP (e.g., Llanillo et al., 2012, 2013; Silva et al., 2009). Since the WOCE program, several expeditions have taken place in offshore locations (oceanic region) of Peru and Chile. Among other measurements, seawater samples were collected and analyzed for their stable isotope composition to serve as a water mass tracers in the region. These tracers offered the opportunity to further improve our understanding of the complex physical processes affecting the water masses and biogeochemical cycles in the region (Druffel & Griffin, 2015; Kumamoto et al., 2011; Martínez-Méndez et al., 2013a; Quay et al., 2003).

Stable isotope ratios of oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) in seawater have been used as a conservative hydrological tracers to determine the advection, mixing, and formation of water masses (Benway & Mix, 2004; Bigg & Rohling, 2000; Conroy et al., 2017; Craig & Gordon, 1965; LeGrande & Schmidt, 2006; Meredith et al., 1999; Schmidt, 1998, 1999). The $\delta^{18}\text{O}$ and δD values and their spatial distribution in the surface ocean are tied to the hydrological cycle through evaporation/precipitation (e.g., Conroy et al., 2013; Tiwari et al., 2013), atmospheric vapor transport (e.g., Benway & Mix, 2004), continental freshwater inputs (e.g., Khatiwala et al., 1999), and sea-ice formation/melting (e.g., Bass et al., 2014; Macdonald et al., 1999). Evaporation preferentially removes the lighter isotopes (^{16}O and ^1H) from the surface ocean layer, causing enrichment of the heavier isotopes (^{18}O and ^2H) as well as an increase in salinity. Precipitation and continental runoff/glacial-ice melting, return freshwater with lighter isotopes back to the ocean (Benway & Mix, 2004; Mackensen, 2001; Mikalsen & Sejrup, 2000). Hence, there are regional linear relationships between $\delta^{18}\text{O}$ and δD and salinity (conservative behavior; Benway & Mix, 2004; Bigg & Rohling, 2000; Conroy et al., 2017; LeGrande & Schmidt, 2006; Schmidt, 1998, 1999).

The stable carbon isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) is a non-conservative tracer, and a semi-quantitative indicator of ventilation and water mass aging (Bostock et al., 2010, 2013; Kroopnick, 1985; Kumamoto et al., 2011). The distribution of $\delta^{13}\text{C}_{\text{DIC}}$ in the surface ocean is controlled by air-sea gas exchange, photosynthesis, carbonate precipitation, and ocean circulation (Gruber et al., 1999; McNeil et al., 2001). During photosynthesis, phytoplankton discriminates ^{12}C against ^{13}C , leaving seawater relatively enriched in ^{13}C leading to higher surface ocean $\delta^{13}\text{C}_{\text{DIC}}$ values, accompanied by low nutrient contents (Gruber et al., 1999). This relationship in surface waters is additionally affected by isotope fractionation that occurs during air-sea CO_2 exchange ($\delta^{13}\text{C}_{\text{air-sea}}$; Broecker & Maier-Reimer, 1992; Charles et al., 1993; Lynch-Stieglitz et al., 1995). For example, the cold temperatures in the surface layers in polar and subpolar regions increase the $\delta^{13}\text{C}_{\text{air-sea}}$ of water masses formed there and this isotopic signature is transferred to the ocean interior upon sinking and conserved until the water masses mix with other water masses (Bostock et al., 2010, 2013; Broecker & Maier-Reimer, 1992; Charles et al., 1993; Charles & Fairbanks, 1990; Oppo & Fairbanks, 1989). Furthermore, as particulate organic matter sinks into the deep ocean, aerobic and anaerobic remineralization within the water column releases ^{12}C and nutrients back to their dissolved inorganic forms ($\delta^{13}\text{C}_{\text{bio}}$). In combination with ocean circulation, $\delta^{13}\text{C}_{\text{DIC}}$ ($\delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{air-sea}} + \delta^{13}\text{C}_{\text{bio}}$) of ocean interior water masses become enriched in ^{12}C en route, a process called water mass “aging,” making older waters carry lower $\delta^{13}\text{C}_{\text{DIC}}$ and higher nutrient contents (Kroopnick, 1985).

Understanding the distribution of $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, and δD in the ocean is important since calcifiers (e.g., foraminifera) found buried in deep sea sediments as well as pore water/algae lipids, recording chemical signals, provide valuable information about past oceanographic environments and conditions.

The study of past water masses geometry and chemistry in the SEP, relies on downcore stable isotope records from calcifiers collected from the shelf and slope of the western continental margin of South America. These allow the reconstructions of density, ventilation, oxygen, and nutrient contents in the water column on various time

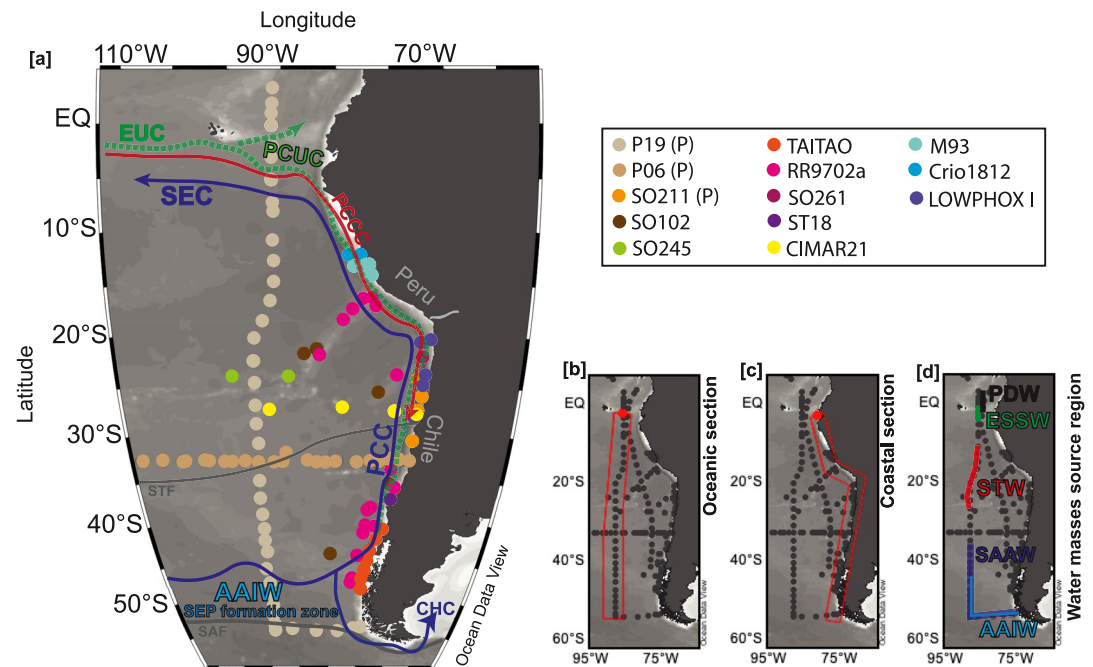


Figure 1. a) Location of the studied hydrological sites (colored dots refer to the individual expeditions listed in the inset and in Table 1). The red polygons in (b) and (c) indicate the meridional oceanic (on average > 1,000 km from the coast) and coastal (on average < 300 km from the coast) sections discussed in this study. Samples between the oceanic and coastal sections are not discussed in this study because they mostly comprise only surface waters and isolated samples from the water column. Features indicated in (a) are main ocean currents, oceanographic fronts, and the Antarctic Intermediate Water (AAIW) formation zone in the Southeast Pacific. Peru-Chile or Humboldt Current (PCC), Peru-Chile Counter Current (PCCC), Peru-Chile Undercurrent (PCUC), Equatorial Undercurrent (EUC), South Equatorial Current (SEC), Cape Horn Current (CHC), Subantarctic Front (SAF), and Subtropical Front (STF). In (d) the regions (colored) along the WOCE line P19, where the source water masses (Table 2) were defined are indicated. The stations of expeditions P19–P06 and SO211 correspond to published stable isotope data from the project GLODAP v2 <https://www.glodap.info/> and Martínez-Méndez et al. (2013a), respectively.

scales (e.g., Haddam et al., 2018, 2020; Martínez-Fontaine et al., 2019; Martínez-Méndez et al., 2013a; Mohtadi et al., 2008; Nürnberg et al., 2015; Siani et al., 2013).

Most of the interpretations from past stable isotope records recovered from the continental shelf and slope in the SEP are based on comparisons with modern oceanographic data from the more oceanic part of the region. This may lead to biased interpretations. Some examples of potential biases are the over/underestimation of (a) changes in past water mass distribution and circulation, due to comparing the extension of a reconstructed water mass in the coastal section with its present extension in the more oceanic region (e.g., De Pol-Holz et al., 2006, 2007); (b) stable isotope disequilibria between water and calcite in proxy calibration studies, due to comparing the stable isotope signature of calcite of coastal samples with water samples collected in the oceanic section (Schmittner et al., 2017), and (c) traceability of regional isotope effects (e.g., biological and physical), which may explain the stable isotope signature of specific water masses (Mackensen, 2001).

Here, for the first time, we combine $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ in seawater to characterize the SEP water masses, using published and new analyses from both the coastal and oceanic regions off Peru and Chile collected between 1992 and 2018. Our collection represents a time snapshot that includes potential seasonal, interannual, and decadal changes of the water masses; this long-term characterization will help to further understand the water masses and the processes, as well as providing calibrations for paleoceanography studies.

2. Regional Setting

2.1. Water Masses and Ocean Circulation

The SEP represents the ocean region from approximately the Equator to 53°S and between the western continental margin of South America and 90°W. It comprises the eastern part of the Equatorial Current System (with eastward and westward currents), eastern part of the South Pacific Subtropical Gyre (SPSG), the eastward West Wind Drift Current which comprises the Peru-Chile Current System (or Humboldt Current System) and the Cape Horn Current (Graco et al., 2013; Grados et al., 2018; Halpin et al., 2004; Stramma et al., 2010; Strub et al., 1998, 2019). Mesoscale surface and subsurface eddies are common, which act as efficient distributors of heat, salt, nutrients, and biomass to the open ocean (Cornejo D'Ottone et al., 2016; Hormazabal et al., 2013; Karstensen & Ulloa, 2009; Morales et al., 2012; Wang et al., 2018). Table S1 shows the acronyms for the individual currents and water masses addressed in this study.

The ocean and coastal regions off Chile and Peru are characterized by five main water masses: Subantarctic Surface Water (SAAW), Subtropical Water (STW), Equatorial Subsurface Water (ESSW), Antarctic Intermediate Water (AAIW), and Pacific Deep Water (PDW; Figures 1 and 2). At the surface, the relatively cold, fresh, oxygenated, $\delta^{13}\text{C}_{\text{DIC}}$ enriched, and low nutrient SAAW is advected equatorward from the Subantarctic Front (SAF) along the eastern part of the SPSG via the Peru-Chile Current (PCC) until $\sim 32^\circ\text{S}$ (Llanillo et al., 2012; Silva et al., 2009). SAAW flowing along the Chilean coast receives freshwater from perennial rivers and meltwater discharges from Patagonian fjords during austral summer (Silva et al., 1997) leading to a fresher SAAW variety (referred to Summer Subantarctic Surface Water, SSAAW; Llanillo et al., 2012). At the Subtropical Front (STF; $35^\circ\text{--}30^\circ\text{S}$) the SAAW subducts into the ocean interior between 50 and 200 m; the subducted SAAW has been named the Eastern South Pacific Intermediate Water (ESPIW; Schneider et al., 2003).

North of 32°S , the surface ocean is occupied by the salty, warm, well-oxygenated STW, characterized by high values of $\delta^{13}\text{C}_{\text{DIC}}$ and low nutrient content. Most of the STW flows with the SPSG, but in the Tropical Eastern Pacific a fraction of STW is advected poleward by the Peru-Chile Counter Current (PCCC; Fiedler & Talley, 2006; Grados et al., 2018; Llanillo et al., 2012; Silva et al., 2009; Tsuchiya & Talley, 1998).

Between 200 and 600 m, the ESSW dominates the water column below the SAAW and STW in the tropical/subtropical SEP. This water mass is characterized by high salinity and nutrient contents, very low oxygen, and low $\delta^{13}\text{C}_{\text{DIC}}$ values (Garcia et al., 2014; Quay et al., 2003; Vargas et al., 2021; Wooster & Gilmartin, 1961). The ESSW derives from the mixing of aged water masses in the (western) Equatorial Pacific and is transported eastward by the Equatorial Undercurrent (EUC). Encountering the Galápagos Archipelago, the EUC deviates south into the SEP shadow zone, characterized by stagnant circulation, which enables further oxygen depletion in the ESSW (Strub et al., 1998). The ESSW is transported poleward along the continental slope by the Peru-Chile Undercurrent (PCUC; also known as the Gunther Undercurrent after Garcia et al., 2014; Llanillo et al., 2013; Wooster & Gilmartin, 1961). During upwelling events, the nutrient-rich ESSW reaches the surface ocean, and thus it is largely responsible for maintaining the high primary productivity and rich fisheries in the region (Montecino & Lange, 2009; Ulloa & Pantoja, 2009). This water mass is associated with the SEP oxygen minimum zone (SEP-OMZ; Silva et al., 2009) and is clearly identified from equatorial latitudes all the way south along the Chilean slope to temperate latitudes (38°S , Llanillo et al., 2012 and 48°S , Silva et al., 2009). Furthermore, south its low oxygen signature disappears through mixing with the SAAW and AAIW below.

At intermediate depths, between 500 and 1,000 m, the AAIW is characterized by relatively low salinity, temperature, and nutrient contents, and high levels of oxygen and $\delta^{13}\text{C}_{\text{DIC}}$ (Bostock et al., 2013; Hanawa & Talley, 2001; Martínez-Méndez et al., 2013a; Silva et al., 2009; Tsuchiya & Talley, 1998). One of the main source regions of AAIW today lies at Subantarctic latitudes close to Southern Patagonia (Hartin et al., 2011) from where the AAIW flows equatorwards at intermediate depths of the eastern boundary current, along the continental slope. Its influence remains still detectable in the equatorial region (Llanillo et al., 2013) albeit weak. AAIW is crucial for the ventilation of the thermocline and intermediate depths of the South Pacific Basin.

At depths $>1,500$ m, PDW dominates; it is characterized by high nutrient and low oxygen contents and low $\delta^{13}\text{C}_{\text{DIC}}$ values (Kumamoto et al., 2011). PDW is the most abundant and oldest water mass worldwide (DeVries, & Holzer, 2019; DeVries, & Primeau, 2011). It derives initially from a complex mixing of Lower Circumpolar Deep Water (LCDW), Antarctic Bottom Water (AABW) with SAAW, AAIW, and North Pacific Intermediate

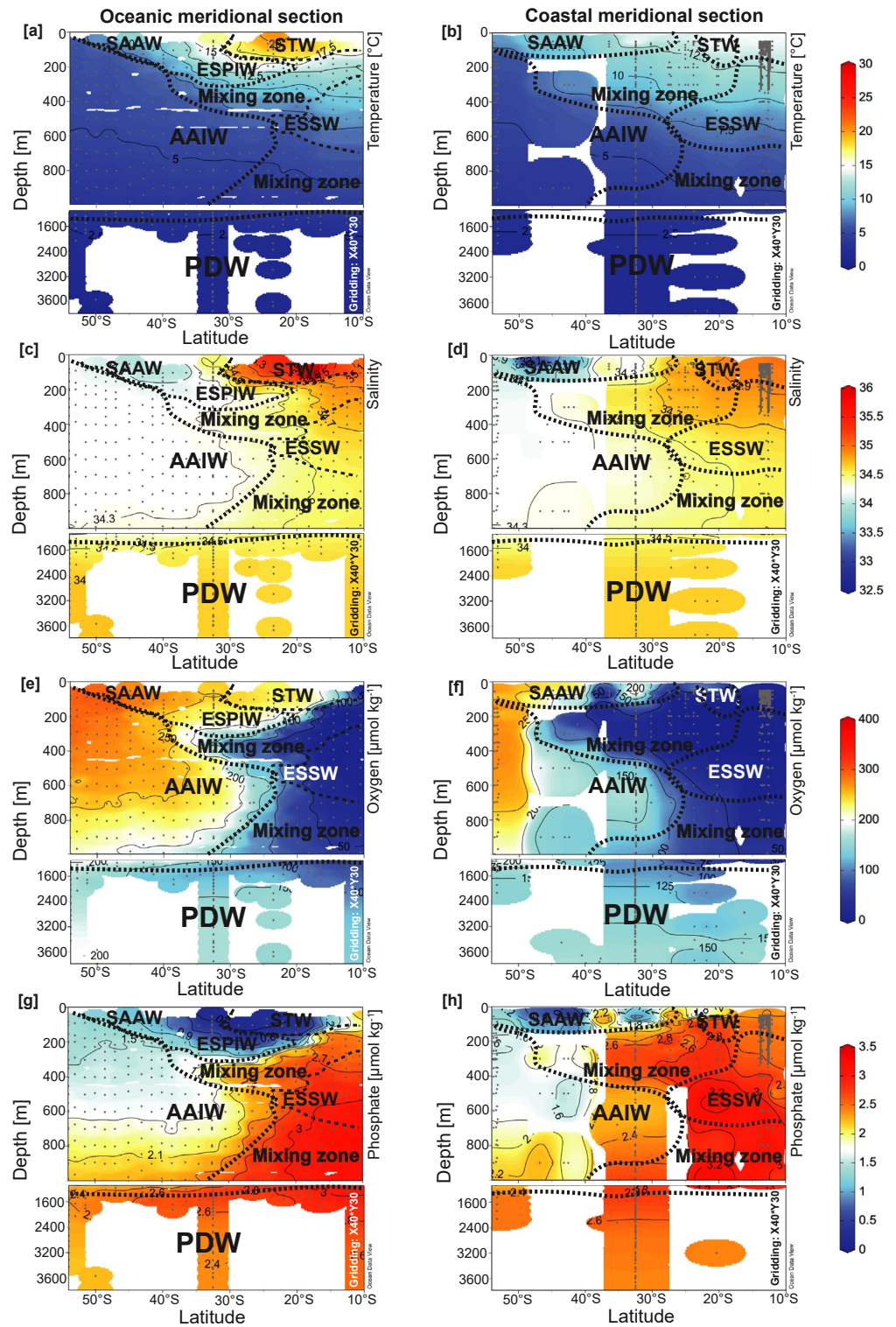


Figure 2. Hydrographic parameters: temperature (a and b), salinity (c and d), oxygen (e and f), phosphate (g and h) in the oceanic and coastal meridional section in the Southeast Pacific. Main water masses can be seen in all sections: SAAW (Subantarctic Surface Water), ESPIW (Eastern South Pacific Intermediate Water), STW (Subtropical Surface Water), ESSW (Equatorial Subsurface Water), AAIW (Antarctic Intermediate Water), and PDW (Pacific Deep Water). Each water sample site is represented by gray dots. The degree of gridding is indicated in the plot. Dashed lines represent the isoline of 50% of the contribution of the water mass to the water mixture. Grey dots show sample sites.

Water (Koshlyakov & Tarakanov, 2004). Along its very long path from high southern latitudes via the North Pacific and before returning south to the SEP, the PDW is further modified by mixing and geothermal warming (Talley, 2013).

Coupled ocean-atmosphere interannual and decadal-scale variations like the El Niño Southern Oscillation (ENSO) and the Pacific Decadal Oscillation (PDO) play a role in altering the mean distribution of the surface and intermediate waters in the SEP (Deutsch et al., 2011; Llanillo et al., 2013; Morales et al., 1999). Llanillo et al. (2013) show that during the warm phases of ENSO (El Niño) and PDO (El Viejo), the core of STW moves closer to the coast displacing ESSW downward and supplying the upper 250 m with oxygen. During the cold phases of ENSO (La Niña) and PDO (La Vieja) intensified upwelling increases the proportion of ESSW in shallower layers, enabling AAIW and ESPIW to concomitantly rise upward and reach further north thereby increasing the oxygenation of the lower part of the SEP-OMZ.

2.2. Upwelling Regime, Mesoscale Structures, and Primary Productivity

Along the western South American coast, the Southeast Pacific Subtropical Anticyclone (SPSA) drives upwelling favorable winds (Bakun & Nelson, 1991). Coastal upwelling causes upward advection of nutrient-rich ESSW, boosting high primary productivity up to $\sim 20 \text{ g C m}^{-2} \text{ day}^{-1}$ in the region (Daneri et al., 2000; Morales, Blanco, et al., 1996; Morales, Braun, et al., 1996; Testa et al., 2018).

The coastal upwelling regime has different spatial and temporal patterns along the western South American margin controlled by the SPSA, local topography, bathymetry, and water column stability (Figueroa & Moffat, 2000; Montecino et al., 2006). Upwelling is largely persistent between 12° and 24°S offshore Peru and northern Chile. However, between 17° and 20°S the Easterly Winds hit the land at a different angle than north or south of this location, therefore upwelling does not occur (e.g., ref. upwelling doldrum zone; Rutllant & Montecino, 2002). Toward the south, the upwelling regime changes from semi-permanent (23°S) to seasonal (33°–37°S; Letelier et al., 2009; Morales, Blanco, et al., 1996; Morales, Braun, et al., 1996). In this region, mesoscale eddies are often formed, changing the structure of the water column and regional biogeochemical cycles (Cornejo D'Ottono et al., 2016; Morales et al., 2012; Stramma et al., 2013).

In northern and southern Patagonia (>40°S) prevailing onshore Westerly winds together with the eastward directed Antarctic Circumpolar Current (Silva et al., 2009) promote downwelling (Shaffer et al., 1995; Strub et al., 1998). However, recent studies have shown that the upwelling/downwelling transition area off 40° and 42°S is shifting southward (Narváez et al., 2019).

Across these upwelling subsystems, maxima in primary productivity occur during austral spring and summer (Morales, Blanco, et al., 1996; Morales, Braun, et al., 1996). Between 30° and 38°S productivity is further fueled by nutrient inputs from river runoff (Masotti et al., 2018; Testa et al., 2018). High primary productivity along the Patagonian region is mainly supported by nutrient inputs brought about by localized rivers and glacier runoff (Pantoja et al., 2011).

3. Materials and Methods

3.1. Water Column CTD and Nutrient Data

In all expeditions (Table 1), Seabird-CTDs attached to Rosettes of Niskin bottles were used to measure conductivity, temperature, pressure, and oxygen. Nutrient samples were siphoned from Niskin bottles into 15 mL plastic vials, measured onboard or stored at -20°C for later measurements. The samples were measured using different autoanalyzer devices, depending on the expedition and laboratory (for further details see Table S2).

3.2. Extended Optimum Multi-Parameter Analysis

The Extended Optimum Multi-Parameter (EOMP) method was used to determine the water mass fractions (%) at each sampling point (Hupe & Karstensen, 2000; Karstensen & Tomczak, 1998). The EOMP is a multidimensional least-square fit that allows obtaining the percentage of mixing of more than three water masses in a water volume. The EOMP takes into consideration the biogeochemical cycling (respiration, remineralization, and denitrification) by including stoichiometry-scaled unknowns for the equation of each non-conservative parameter (Hupe

Table 1
Metadata of the Expeditions Providing the Sample Material and Data for This Study

Expedition ID	Research vessel ID	Sampling date (day/ month/year)	Longitude ranges (degrees east)	Latitude ranges (degrees north)	Data provided by	Measurements
TAITAO	R/V Cabo de Hornos	01/11/2018 to 13/11/2018	−74.79 to −75.81	(−41.75) to (−47.66)	This study	$\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, δD , N, O_2 , TSD
SO-261	R/V SONNE	06/03/2018 to 22/03/2018	(−70.88) to (−71.51)	(−21.82) to (−23.88)	This study	$\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, δD , O_2 , TSD
SO-245	R/V SONNE	25/12/2015 to 30/12/2015	(−84.56) to (−90.03)	(−21.82) to (−23.88)	This study	$\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, δD , N*, O_2 *, TSD*
316N138-3 (P06)	R/V Knorr	30/05/1992 to 06/06/1992	(−71.67) to (−96.67)	(−32.48) to (−32.51)	WOCE, 1992	$\delta^{13}\text{C}_{\text{DIC}}$ *, N*, O_2 *, TSD*
49NZ20030909 (P06)	R/V Mirai	03/08/2003 to 16/10/2003	(−72.71) to (−98.66)	(−32.49) to (−32.50)	WOCE, 2003	$\delta^{13}\text{C}_{\text{DIC}}$ *, N*, O_2 *, TSD*
318M20100105 (P06)	R/V Melville	05/01/2010 to 1/02/2010	(−71.92) to (−100.56)	(−32.49) to (−32.50)	WOCE, 2010	$\delta^{13}\text{C}_{\text{DIC}}$ *, N*, O_2 *, TSD*
LOWPHOX 1	R/V Cabo de Hornos	11–12/2015	(−70.51) to (−71.34)	(−20.1) to (27.66)	This study	$\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, N, O_2 , TSD
RR9702a	R/V Roger Revelle	2–4/1997	(−73) to (−81.5)	(−13.70) to (−47)	This study	$\delta^{13}\text{C}_{\text{DIC}}$, O_2
SO-102	R/V SONNE	09/05/1995 to 28/06/1995	(−72.81) to (−82.91)	(−21.08) to (−43.24)	This study	$\delta^{13}\text{C}_{\text{DIC}}$, N, O_2 , TSD
SO-211	R/V SONNE	10/11/2010 to 26/11/2010	(−70.65) to (−71.77)	(−23.85) to (−30.24)	This study	$\delta^{13}\text{C}_{\text{DIC}}$ *, $\delta^{18}\text{O}$, O_2 , TSD
Station18-Udec	L/C Kay Kay II	19/05/2015 and 23/06/2015	−73	−36.50	This study	$\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, N, O_2 , TSD
CIMAR-21	R/V Cabo de Hornos	12/10/2015 to 20/10/2015	(−71.25) to (86.8)	(−27.09) to (−27.24)	This study	$\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, N**, O_2 **, TSD**
Crio1812	R/V Jose Oyala	27/12/2018 to 28/12/2018	(−77.22) to (−78.85)	−12	This study	$\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, δD , N, O_2 , TSD
316N138_12 (P19)	R/V Knorr	22/02/1993 to 13/04/1993	(−75.02) to (−88)	(−8) to (−54)	WOCE, 1993	$\delta^{13}\text{C}_{\text{DIC}}$ *, N*, O_2 *, TSD*
M93	R/V Meteor	06/02/2013 to 10/03/2013	(−76) to (−78)	(−12) to (−13)	This study	$\delta^{13}\text{C}_{\text{DIC}}$, N*, O_2 *, TSD*

Note. Type of data and samples obtained per expedition are indicated in Tables S1–S3. N: Nutrients; TDS: Temperature, salinity, and density. * SO245 (Ferdelman et al., 2019), SO211 (Martínez-Méndez et al., 2013b, 2013c, 2013d, 2013e), M93 (Lavik & Krahnmann, 2016). **CIMAR21 data set from shallow water depth is available in Farías and Troncoso (2021), in this study we add information about deep stations. * and ** data sets are available in GLODAP and PANGAEA webpages.

& Karstensen, 2000). The parameters used for the EOMP analysis are potential temperature, salinity, oxygen, and inorganic nutrients (phosphate, silicate, and nitrate; Hupe & Karstensen, 2000; Karstensen & Tomczak, 1998; Poole & Tomczak, 1999). The EOMP analysis requires a correct definition of the source water masses expected to contribute to the observed parameter in the water mixture. The source regions (Figure 1c) for the five main water masses addressed in this study are summarized in Section 2.1 (Table 1).

We used the potential temperature, salinity, oxygen, silicate, and nitrate end-members calculated for SAAW, STW, ESSW, AAIW, and PDW by Llanillo et al. (2013; Table 2) assuming that the source waters are in a theoretical steady state. Hence, changes in the water mass fractions and their biogeochemical signals are interpreted as responding solely to the redistribution of water masses and to different biogeochemical cycling (remineralization and denitrification).

Before resolving the EOMP, the different parameters are normalized and weighted in order to control their relative influence on the solution (Tomczak & Large, 1989). The largest weights are assigned to mass conservation (i.e., the mass conservation equation will be more relevant for the resolution of the EOMP) and to the parameters with the largest sampling accuracy (potential temperature and salinity). For potential temperature and salinity the assigned weight was 24. Nutrients, such as phosphate, nitrate, and nitrite have weights of 7. Due to a non-constant

Table 2
Southeast Pacific Source Water Mass Types (Figure 1d) Used for the EOMP Analysis to Obtain $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, and δD End-Members

Water mass	Pot. Temp. (°C)	Salinity	Oxygen ($\mu\text{mol kg}^{-1}$)	Phosphate ($\mu\text{mol kg}^{-1}$)	Silicate ($\mu\text{mol kg}^{-1}$)	Nitrate ($\mu\text{mol kg}^{-1}$)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\delta^{18}\text{O}$ (‰)	δD (‰)
STW	20.80	35.52	240.65	0.46	2.23	0.74	0.42	0.60	3.22
SAAW	11	34	268.20	1.07	2.17	13.70	1.81	-0.12	-1.17
ESSW	10	34.80	13.60	2.43	29.81	32.70	-0.48	0.31	0.82
AAIW	3.00	34	238.20	1.97	24.60	28.50	1.59	0.00	-1.01
PDW	1.82	34.67	105.20	2.76	157.30	38.42	0.04	0.01	-1.28
Weight	24	24	7	7	3.5	7	-	-	-

Note. The source water masses are Subtropical Surface Water (STW), Subantarctic Surface Water (SAAW), Equatorial Subsurface Water (ESSW), Antarctic Intermediate Water (AAIW), and Pacific Deep Water (PDW). The water type values and weights (bottom row) of potential temperature, salinity, oxygen, phosphate, silicate, and nitrate concentrations were obtained from Llanillo et al. (2013). The variables considered conservative are potential temperature, salinity, $\delta^{18}\text{O}$, and δD . Oxygen, phosphate, silicate, nitrate, and $\delta^{13}\text{C}_{\text{DIC}}$ parameters were considered non-conservative.

relationship during remineralization with phosphate and nitrate, silicate was assigned with half of the nutrient weight (3.5; Llanillo et al., 2013; Table 2).

The EOMP analysis was applied to the full data set including the oceanic and coastal hydrological sections (Figure 1), excluding those data points located within the uppermost 55 m of the water column that correspond to an average mixed layer estimated for the study area (Leth et al., 2004; Llanillo et al., 2013). As mixed layer points are influenced by air-sea interaction processes, they cannot be resolved with the EOMP (i.e., potential temperature and salinity are not conservative).

Only data points with a mass conservation error <4% were selected for this study and, consequently, this can be interpreted as the uncertainty associated with the EOMP results. In 1,094 out of 2,680 data points it was possible to apply the EOMP analysis. 40% of the data qualify for EOMP analyses, providing new insights into the oceanography of this region with the largest dataset for the SEP so far.

3.3. Water Column Stable Isotope Data

Water samples for $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ were collected during several expeditions conducted between 1992 and 2018 in the SEP using Niskin bottles coupled in a Rosette with CTD device (see Table S3 and S4). The RR-9702a expedition is an exception; a single Niskin bottle was coupled to the top of a multicorer device. To prevent contamination and/or micro-evaporation, water samples were immediately siphoned from Niskin bottles into 100 and 25 mL glass and polypropylene bottles avoiding bubbles. Water samples for $\delta^{13}\text{C}_{\text{DIC}}$ determinations were poisoned onboard with 0.5 mL of ultra-saturated mercury chloride (HgCl_2) to avoid alternating the $\delta^{13}\text{C}_{\text{DIC}}$ signature by further remineralization. All $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ samples were sealed with parafilm and kept at 4°C until analysis in the laboratory.

3.3.1. Water Column $\delta^{18}\text{O}$ and δD Analyses

The $\delta^{18}\text{O}$ ($n = 200$, 8 expeditions) and δD ($n = 90$, 8 expeditions) compositions of water samples were determined at MARUM-Bremen, CEOAS-Oregon, and BGS-Nottingham laboratories (see Tables 1 and S3). At MARUM-Bremen, dual $\delta^{18}\text{O}$ - δD analyses were conducted using a Picarro L-2130i performing nine injections per sample. The first seven injections were ignored to preclude memory effects that potentially might occur in continuous runs of several samples. Results obtained were normalized to VSMOW2 through repeated analyses of house standards as SLAP2 (Standard Light Antarctic Precipitation 2; $\delta^{18}\text{O}$: $-55.5 \pm 0.02\text{‰}$, δD : $-427.5 \pm 0.3\text{‰}$; IAEA, 2017) and VSMOW2 (Vienna Standard Mean Ocean Water; $\delta^{18}\text{O}$: $0 \pm 0.02\text{‰}$, δD : $0 \pm 0.3\text{‰}$; IAEA, 2017). Measurement errors for all samples were about 0.08‰ for $\delta^{18}\text{O}$ and 0.2‰ for δD .

At CEOAS-Oregon and BGS-Nottingham $\delta^{18}\text{O}$ analyses were done by isotope ratio (dual inlet) mass spectrometry using a DeltaPlus X and Isoprime 100 mass spectrometer plus Aquaprep device, respectively. Both

Table 3
Mean and Standard Deviation ($\mu \pm 1\sigma$) in the 50% Contribution Isoline of Each Main Water Mass to the Water Mixture in the Coastal and Ocean Section

Water mass	Temperature (°C)	Salinity	Oxygen ($\mu\text{mol kg}^{-1}$)	Silicate ($\mu\text{mol kg}^{-1}$)	Phosphate ($\mu\text{mol kg}^{-1}$)	Nitrate ($\mu\text{mol kg}^{-1}$)	Nitrite ($\mu\text{mol kg}^{-1}$)	$\delta^{18}\text{O}$ (‰)	δD (‰)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\delta^{13}\text{C}_{\text{air-sea}}$ (‰)
STW coast	14.03 ± 1.18	34.93 ± 0.08	11.20 ± 9.93	22.73 ± 5.20	2.67 ± 0.47	16.85 ± 6.82	1.34 ± 2.13	0.32 ± 0.17	1.61 ± 0.12	-0.41 ± 0.32	0.04 ± 0.48
STW ocean	17.47 ± 1.08	35.11 ± 0.19	207.17 ± 56.03	3.33 ± 3.62	0.64 ± 0.54	4.78 ± 7.72	0.13 ± 0.26	-	-	1.59 ± 0.46	-0.43 ± 0.14
SAAW coast	10.97 ± 1.75	34.10 ± 0.21	190.73 ± 56.93	5.12 ± 4.43	1.34 ± 0.51	14.40 ± 6.38	0.12 ± 0.11	-0.10 ± 0.25	-0.13 ± 0.39	1.16 ± 0.46	-0.03 ± 0.37
SAAW ocean	11.63 ± 2.36	34.28 ± 0.19	229.62 ± 38.07	2.87 ± 2.12	1.00 ± 0.39	11.85 ± 5.98	0.12 ± 0.19	-	-	1.48 ± 0.26	-0.08 ± 0.33
ESSW coast	10.87 ± 2.27	34.74 ± 0.19	18.64 ± 26.58	25.44 ± 5.87	2.57 ± 0.30	25.94 ± 7.91	2.15 ± 2.29	0.30 ± 0.25	1 ± 0.79	-0.07 ± 0.31	0.52 ± 0.12
ESSW ocean	9.8 ± 2.22	34.70 ± 0.16	24.54 ± 30.67	34.68 ± 12.30	2.65 ± 0.33	34.97 ± 5.50	0.01 ± 0.03	-	-	0.19 ± 0.23	0.32 ± 0.35
AAIW coast	5.05 ± 0.74	34.26 ± 0.08	212.81 ± 54.27	19.82 ± 11.24	1.97 ± 0.34	27.53 ± 5.57	0.04 ± 0.09	-0.02 ± 0.16	-0.55 ± 0.58	1.01 ± 0.29	0.54 ± 0.28
AAIW ocean	5.23 ± 0.92	34.26 ± 0.05	241.16 ± 43.62	17.47 ± 11.14	1.82 ± 0.31	26.03 ± 4.61	0.02 ± 0.08	-	-	1.14 ± 0.30	0.53 ± 0.17
PDW coast	2.24 ± 0.54	34.63 ± 0.06	140.17 ± 20.34	112.05 ± 17.01	2.57 ± 0.14	36.36 ± 2.10	0.01 ± 0.02	-	-	0.20 ± 0.09	0.43 ± 0.23
PDW ocean	2.86 ± 0.82	35.59 ± 0.07	120.75 ± 39.09	103.79 ± 22.95	2.70 ± 0.26	38.06 ± 2.95	0.00 ± 0.00	-	-	0.19 ± 0.20	0.44 ± 0.22

Note. For $\delta^{18}\text{O}$ and δD in the water masses from the oceanic section and for the PDW in the coastal section the data was not sufficient for the analysis.

laboratories followed the water- CO_2 equilibration method modified by Epstein and Mayeda (1953). Working standards SLAP2 and GISP (Greenland Ice Sheet Precipitation; $\delta^{18}\text{O}$: $-24.76 \pm 0.09\text{‰}$, δD : $-189.5 \pm 1.2\text{‰}$, IAEA, 2017) indicate measurement errors at $<0.05\text{‰}$ for $\delta^{18}\text{O}$ and the results were corrected to VSMOW.

3.3.2. Water Column $\delta^{13}\text{C}_{\text{DIC}}$ Analyses

The $\delta^{13}\text{C}_{\text{DIC}}$ ($n = 279$, 10 expeditions) samples were prepared and analyzed at MAR-UM-Bremen, WHOI-Massachusetts, and the Museum für Naturkunde-Berlin laboratories (see Tables 1 and S4). Preparation involved the injection of an aliquot of 2 mL of seawater through a septum into a vial with 1 mL concentrated phosphoric acid flushed with pure helium. The resulting full batch of samples was kept at room temperature for at least 6 hr to enable full reaction between the DIC and the acid to produce CO_2 . $\delta^{13}\text{C}_{\text{DIC}}$ were determined using a Thermo Fisher Gas Bench II coupled to a Thermo Finnigan MAT 252 mass spectrometer and Thermo Fisher Scientific Delta V. The standard deviation for all laboratories was based on routine measurements of the internal standard Ground Solnhofen Limestone-SHK Br2008 ($\delta^{13}\text{C}$: -0.96‰) and was better than 0.1‰ . Working standards were calibrated against NBS 19 ($\delta^{13}\text{C}$: $+1.95\text{‰}$; Brand et al., 2014), NBS 18 ($\delta^{13}\text{C}$: -5.01 ± 0.03 ; Brand et al., 2014). All results were then corrected to VPDB. To complement our new data, we include in the database the published $\delta^{13}\text{C}_{\text{DIC}}$ values for the SEP ($n = 1552$, 4 expeditions, see Table S4). This data was prepared following the WOCE protocols and the data are stored in the GLODAP database <https://www.glodap.info/>.

The burning of fossil fuels since the Industrial Revolution has led to the long-term depletion of $\delta^{13}\text{CO}_2$ in the atmosphere, which in turn is affecting seawater $\delta^{13}\text{C}_{\text{DIC}}$ values (e.g., ref. Suess Effect; Keeling, 1979; Suess, 1955). The maximum Suess effect in the SEP is found in surface waters reaching between -0.6‰ and -0.4‰ at 100 m, -0.4‰ and -0.2‰ at 200 m, -0.2‰ and -0.05‰ at 300–400 m. Below 800 m no depleted $\delta^{13}\text{CO}_2$ has been registered so far (Eide et al., 2017). The maximum Suess effect in SEP waters has been computed by global compilations which only consider the regional P06 WOCE line expeditions from 1992, 2003, and 2010 (316N138-3/49NZ20030303/318M20100105). Due to the low amount of temporal and spatial $\delta^{13}\text{C}_{\text{DIC}}$ data for the SEP used for Suess effect estimations, in this study the corrections are not applied. We provide raw data from 1992 to 2018 which offer an accurate distribution of the tracers that can be used as a modern analogue for regional paleoceanographic reconstructions.

3.3.3. $\delta^{13}\text{C}$ From Air-Sea Exchange ($\delta^{13}\text{C}_{\text{air-sea}}$)

For the samples with $\delta^{13}\text{C}_{\text{DIC}}$ and phosphate measurements, the $\delta^{13}\text{C}_{\text{air-sea}}$ exchange values were calculated (Table 3) based in the equation proposed by Broecker and Maier-Reimer (1992) and reviewed by Lynch-Stieglitz et al. (1995). $\delta^{13}\text{C}_{\text{air-sea}}$ explains how much a water mass can be affected by the fractionation of carbon isotopes in surface waters due the exchange of CO_2 between the atmosphere and the surface ocean. To calculate $\delta^{13}\text{C}_{\text{air-sea}}$ the $\delta^{13}\text{C}_{\text{DIC}}$ values are corrected using the Redfield relationship from the deep Pacific/Indian Ocean:

$$\delta^{13}\text{C}_{\text{air-sea}} = \delta^{13}\text{C}_{\text{DIC}} + 1.11 \times \text{PO}_4 - 2.7$$

3.3.4. Stable Isotope End-Member Calculations

Once the composition of the water mixture at each sampled point was calculated using the EOMP, the source water types (i.e., end-members) of $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ values for each water mass were computed by resolving (through least-squares) in a system of linear equations (one per sampled point with EOMP solution) with the unknowns being now the isotopic end-members and the coefficients being the previously computed water mass contribution in each sampled point. The maximum error of the EOMP analysis is

4%. Because $\delta^{13}\text{C}_{\text{DIC}}$ is considered a non-conservative tracer, the system of equations includes the remineralization and denitrification as coefficients previously computed by Llanillo et al. (2013).

3.4. Water Mass Temperature, Salinity, Nutrients, and Stable Isotope Statistical Analyses

The values considered for statistical analyses (mean and standard deviation, $\mu \pm 1\sigma$) only reflect samples marked by a dominant water mass (>50% contribution, calculated using EOMP analysis) and which are from below the mixed layer (>55 m).

Because of this criteria no statistical analyses were carried out for $\delta^{18}\text{O}$ and δD of the oceanic section. Temperature, salinity, oxygen, nutrients (phosphate, nitrate, nitrite, and silicate), and $\delta^{13}\text{C}_{\text{DIC}}$ data did not meet this criteria for the oceanic and coastal sections. Table 3 and Figures S1–S9, summarized the $\mu \pm 1\sigma$ results for all hydrological parameters classified by water mass and region.

To assess whether it is possible to use the $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ to trace water masses through paleoceanographic reconstructions, we statistically differentiate the signatures of the main water masses in the SEP using histograms (Figures S8 and S9) and non-parametric Mann-Whitney pairwise testing. These analyses clearly distinguish the degree of overlap between tracer values of the individual water mass.

3.5. Data Visualization and Processing

For data visualization we use Ocean Data View 5.2.1 (Schlitzer, 2021; <https://odv.awi.de/>). The original data for the meridional section plots were gridded using interpolated variational analysis (DIVA, <https://github.com/gher-ulg/DIVA>) and weighted-average interpolation. The degree of gridding was maximum 35 in the coordinate axis (X) and 45 in the axis (Y). For the EOMP analysis, a MATLAB code was developed by Llanillo et al. (2012, 2013).

A Python code was developed for statistical analyses and data manipulation using elements of the free and open-source library SciPy for scientific and technical computing <https://www.scipy.org/>. For further information see <https://github.com/Paleobiogeochemistry>.

4. Results and Discussion

We present the first isotope characterization of the main water masses of the SEP in order to validate $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ as past water mass tracers (i.e., proxies). Our work provides unique information that compiles a long-term data set of 20 yr, serving as the first isotopical geochemical baseline for future initiatives aimed at testing detailed paleoceanographic dynamics in the SEP.

4.1. Distribution and Mixing of Southeast Pacific Water Masses

Our EOMP analysis reveals that north of $\sim 30^\circ\text{S}$ STW dominates in the oceanic section in the upper 200 m, contributing >60% to the water mixture (Figure 3a). In the coastal section, STW contributes only 40%–50% of the water mass (Figure 3b) due to horizontal mixing with SAAW and vertical mixing (upwelling) with ESSW (Figures 3b and 3f), confirming results by Silva et al. (2009).

South of $\sim 25^\circ\text{S}$, the SAAW contributes between 60% and 90% to the water mixture in the upper 300 m of the oceanic section and it subducts below the STW (Figure 3c). After the subduction, when the SAAW has become the ESPIW, its core (>50%, at ~ 200 m) can be traced until 20°S . Luyten et al. (1983), Schneider et al., (2003) and Hernández-Vaca et al. (2017) propose that SAAW is subducted into the ocean interior along the Subtropical Front due to wind-induced Ekman pumping. In the coastal section, SAAW dominates as a surface water mass as far north as $\sim 30^\circ\text{S}$, without being subducted beneath the STW. We hypothesize that three processes prevent intense downwelling of the SAAW near the coast (a) riverine freshwater input along the coastal section, (b) coastal upwelling, and (c) the position further north of the Subtropical Front in the Chilean coast.

In the subsurface below STW and SAAW, ESSW can be found in the northern part of the whole SEP, cradling above and alongside AAIW between 100 and 700 m. Here ESSW makes up 50%–70% of the water mixture with its core centered at 500 m. The ESSW flows southward and is mixing with SAAW (above) and AAIW (below).

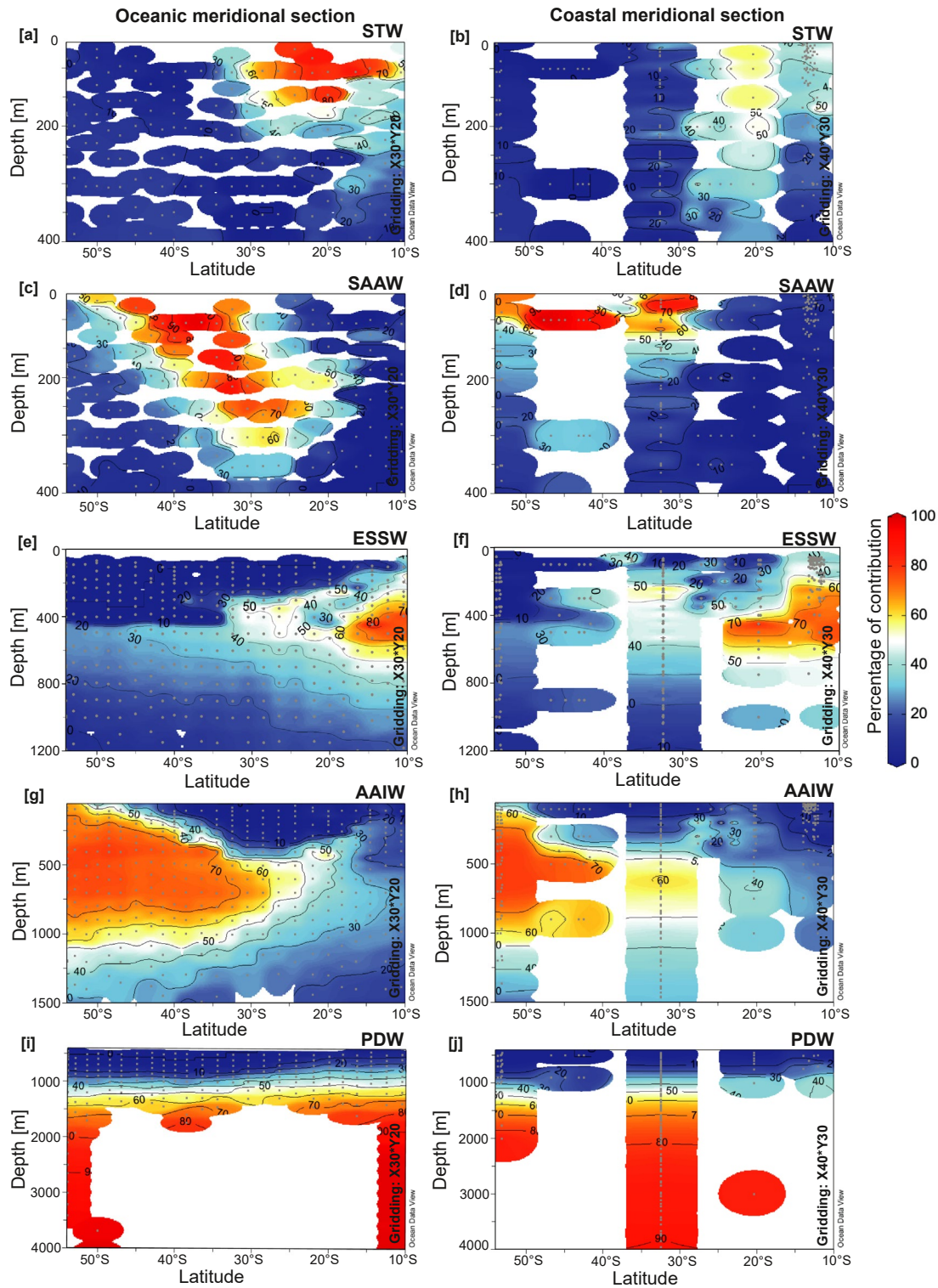


Figure 3. Relative water mass contribution from the water mixture in percentage (%) presented along the oceanic and coastal hydrological sections. Results were obtained using the extended optimum multiparameter (EOMP) analysis with the source water mass characteristics given in Table 3. The representation of the percentage distribution for each water mass is from top to bottom as STW (Subtropical Surface Water; (a) Oceanic section, (b) Coastal section), SAAW (Subantarctic Surface Water; (c) Oceanic section, (d) Coastal section), ESSW (Equatorial Subsurface Water; (e) Oceanic section, (f) Coastal section), AAIW (Antarctic Intermediate Water; (g) Oceanic section, (h) Coastal section), and PDW (Pacific Deep Water; (i) Oceanic section, (j) Coastal section). Each site is represented by gray dots. The degree of gridding is indicated in the sections. Samples from the mixed layer (uppermost 55 m) were not included in the analysis. Grey dots show sample sites.

While this mixing is limited to $\sim 20^\circ$ to 30°S in the oceanic section (Figures 3e–3f), ESSW is prominent (30% and 50%) in the coastal section as far south as 40°S (Figures 3f and S3 at 50 m) with an upward expansion to 100 m water depth.

At the coastal section off Peru and northern Chile upwelling brings the ESSW closer to the surface. It also reaches a more southern position due to hydrostatic equilibrium where low ESPIW-SAAW contributions to depths >100 m allow ESSW to advance further south, transported by the PCUC along the continental slope until it is mixing with the AAIW and SAAW. Silva et al. (2009) found a much higher maximum contribution of $>90\%$ of the ESSW between 30° and 10°S between 100 and 500 m water depth in the oceanic section.

Beneath the SAAW and ESSW (54° – 25°S), the northward flowing AAIW contributes between 70% and 50% to the water mixture down to depths of 1,200 m, both in the oceanic and coastal sections. In the south, the core of the AAIW is centered at ~ 600 m with a water column range between ~ 200 and ~ 800 m. Furthermore north, AAIW deepens to 400–800 m in the coastal section, whereas in the oceanic section it remains at a similar depth as in the south of the study region (Figures 3g and 3h). AAIW still contributes $>50\%$ at 20°S (oceanic section) and 25°S (coastal section), respectively, and becomes less important ($<30\%$) between 20° and 15°S (oceanic and coastal sections; Figures 3g and 3h).

The water mass contribution results show that there are differences between the coastal and oceanic section above 1,000 m water depth (Figure 3). In the coastal section the STW has less predominance and mixes with the upper part of the ESSW. We observe that the ESSW can extend to southern latitudes than in the oceanic section. As well, we find that between the ESSW and the upper part of the AAIW is defined a large mixing zone that is not observed in the oceanic sections.

Toward deeper levels in the water column between 1,000 and 4,000 m, the PDW contributes progressively from 40% to 90% to the water mixture (Figures 3i and 3j). An upper (1,000–1,500 m) and a lower PDW ($>1,500$ m) can be separated by density; the upper horizon actively mixes with AAIW and ESSW whereas lower PDW is much purer. Our limited data suggests that there are no differences in PDW contribution offshore and onshore. Insufficient data prevents us from considering CDW in the extended EOMP analysis.

4.2. Water Mass Characterization for the Southeast Pacific Using Stable Isotopes of Oxygen, Hydrogen, and Carbon

4.2.1. Conservative Water Mass Tracers: Oxygen and Hydrogen Isotopes

The characterization of SEP water masses by $\delta^{18}\text{O}$ and δD is limited to the coastal section due to the scarcity of data in the oceanic section (Figures 4c–4f). For PDW it was not possible to calculate the mean and standard deviation ($\mu \pm 1\sigma$) due to the limited data availability.

The STW, SAAW, ESSW and AAIW maintain their source region $\delta^{18}\text{O}$ and δD (Figures 1d; Tables 2 and 3). The relatively heavy STW isotopic composition (Figures 5 and S8; Table 2) suggests that this water mass originates from a region with high evaporation rates (Conroy et al., 2017). This is consistent with earlier work showing that the STW is formed in the northern part of the high-pressure Subtropical Pacific Gyre region (Stramma et al., 1995; Wyrki, 1973). Because of the hyperarid climate in southern Peru/northern Chile, the limited discharge of freshwater indeed does not affect the $\delta^{18}\text{O}$ and δD signature of the broader STW. However, the isotopic values combined with temperature and salinity, provide evidence that STW is mixed with upwelled ESSW between 10° and 32°S (Figures 4b, 4d, 5g, and 5h).

The SAAW has comparably low $\delta^{18}\text{O}$ and δD values (Figure 4b, 4d, 5g, and 5h; Table 2). This is related to high rates of precipitation over the Subantarctic Zone (Bass et al., 2014) and the input and subsequent mixing of freshwater coming from discharge of meltwater directly from the humid southern Patagonian glaciers. Temperature/salinity diagrams of the oceanic (Figure 5a) and coastal (Figures 5g and 5h) sections, clearly reveal that coastal SAAW is fresher than its oceanic counterpart, indicating the dominance of the SSAW (Davila et al., 2002; Llanillo et al., 2012; Rojas & Silva, 1996; Silva et al., 2009; Silva & Neshyba, 1979/1980).

Similar to STW, the ESSW is marked by relatively high isotopic values, indicating that it is formed in the Equatorial Pacific region where evaporation exceeds precipitation. Once ESSW mixes with AAIW and SAAW off central-southern Chile, its values become modified (Figure 4b, 4d, 5g, and 5h; Table 2).

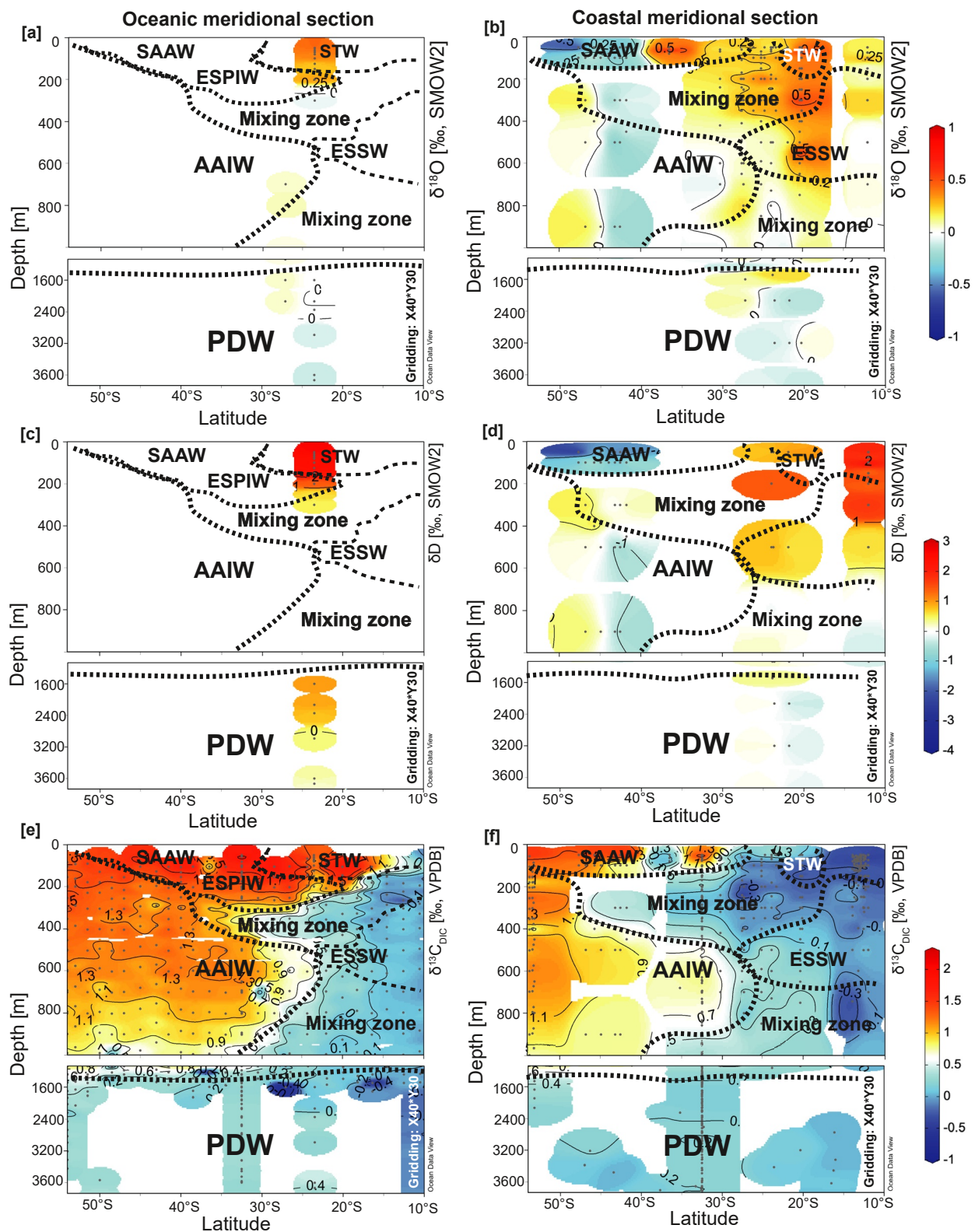


Figure 4. $\delta^{18}\text{O}$ (a and b), δD (c and d), and $\delta^{13}\text{C}_{\text{DIC}}$ (e and f) oceanic-coastal meridional sections in the Southeast Pacific. Main water masses can be seen in all the hydrological sections: STW (Subtropical Surface Water), SAAW (Subantarctic Surface Water), ESPIW (Eastern South Pacific Intermediate Water), ESSW (Equatorial Subsurface Water), AAIW (Antarctic Intermediate Water), and PDW (Pacific Deep Water). Small gray dots represent the sampling site. The degree of gridding is indicated in the sections. Dashed lines represent the isoline of 50% of the contribution of the water mass to the water mixture. Grey dots show sample sites.

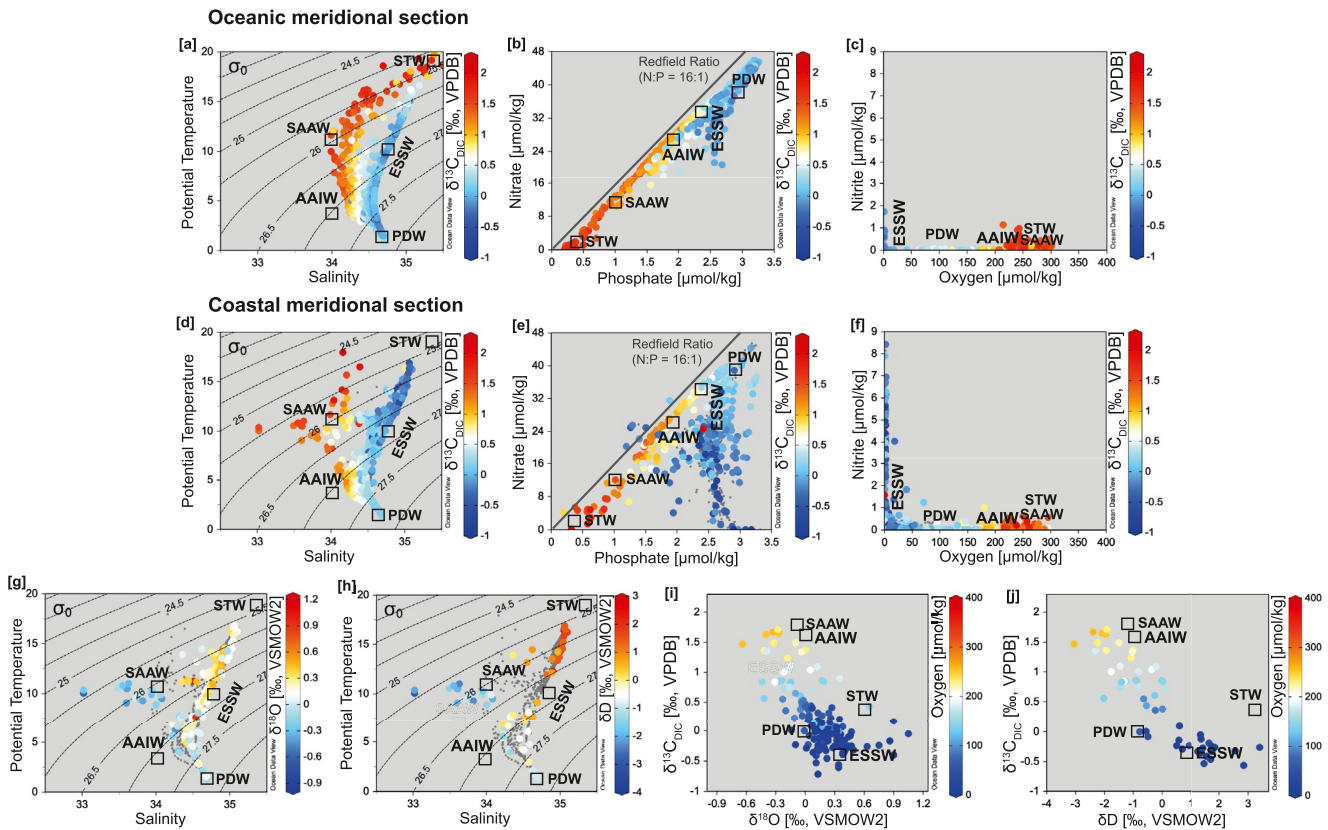


Figure 5. (a, d, g, and h) Potential temperature-salinity with density isopycnals. (b and e) Nitrate-Phosphate diagram, with Redfield ratio shown by a gray line. (c and f) Nitrite-Oxygen diagrams from the oceanic and coastal sections. (i and j) $\delta^{13}\text{C}_{\text{DIC}}-\delta^{18}\text{O}$ diagram. The figures are color-coded from (a) to (f) by $\delta^{13}\text{C}_{\text{DIC}}$ in (g) by $\delta^{18}\text{O}$ in (h) and by δD in (i and j) by oxygen concentrations. Water mass end-members characteristics are shown in black squares: STW (Subtropical Surface Water), SAAW (Subantarctic Surface Water), ESSW (Equatorial Subsurface Water), AAIW (Antarctic Intermediate Water), and PDW (Pacific Deep Water). Grey dots show sample sites.

The AAIW, as the SAAW, is formed in the southern section of the SEP (McCartney, 1977) and travels North toward the tropical east Pacific (Llanillo et al., 2018; McCartney, 1977). Its $\delta^{18}\text{O}$ value (Table 2) is similar to those reported previously for surface waters at the Subantarctic front (Bass et al., 2014; $\delta^{18}\text{O}$: -0.3‰ and δD : 0‰) implying that AAIW is also influenced by high oceanic precipitation. Slightly depleted δD values of AAIW could also result from the contribution of melting ice from the Patagonian Fjords.

Because there were only a few data points for PDW in the SEP we were not able to calculate mean and standard deviations ($\mu \pm 1\sigma$). Hence, these data should be taken with caution.

4.2.2. $\delta^{18}\text{O}$ -Salinity and δD -Salinity Relationships in the Southeast Pacific

In the modern regional ocean, $\delta^{18}\text{O}$ -salinity ($\delta^{18}\text{O}$ -S) and δD -salinity (δD -S) relationships are used for understanding the ocean and atmosphere forcings that influence these, to enable potential reconstructions of past regional hydrographies (Benway & Mix, 2004; Bigg & Rohling, 2000; Conroy et al., 2017; LeGrande & Schmidt, 2006; Schmidt, 1998, 1999). LeGrande and Schmidt (2006) and Schmidt (2009) classified $\delta^{18}\text{O}$ -salinity slopes and intercepts from surface waters from several regions worldwide. These authors concluded that steep slopes (around $0.5\text{‰}/\text{sal}$) and low intercepts (around -15‰ and -17‰) characterize mid- and high-latitudes, where the $\delta^{18}\text{O}$ end-member of freshwater is controlled by local precipitation. In tropical regions, the $\delta^{18}\text{O}$ end-member is primarily controlled by evaporation. Therefore, the $\delta^{18}\text{O}$ signature in the lower latitudes is isotopically heavier due to the effect of evaporative fractionation. Slopes and intercepts for the respective $\delta^{18}\text{O}$ -S relationship tend to be flat ($0.1\text{‰}/\text{sal}$ – $0.3\text{‰}/\text{sal}$) and higher (from about -8‰ to -10‰).

There are no published δD -S relationships for the Pacific Ocean and our δD data set is small, therefore the main discussion is mostly based on the relationship between $\delta^{18}\text{O}$ and salinity. We are aware that our $\delta^{18}\text{O}$ -S and δD -S

Table 4

$\delta^{18}\text{O}$ -Salinity, δD -Salinity Relationships Results (Slopes, Intercepts, r^2 , and p -Value) Determined for the Main Water Masses at the Southeast Pacific Compared With Published Data

Region or Water Mass	Year of sampling	Data points		Slope		Intercept		r^2		p -Value	
		$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD
This study											
SAAW	2010–2018	8	7	0.81	1.04	−27.54	−36.49	0.57	0.15	0.03	0.39
ESSW	2010–2018	22	9	−0.08	4.12	2.97	−142.43	0.00	0.55	0.83	0.02
Published data											
South Pacific (Schmidt, 1999)				0.63		−21.5		0.78			
Equatorial east Pacific (Schmidt, 1999)				0.10		−3.3		0.35			
Northeast Pacific (Schmidt, 1999)				0.37		−12.9		0.96			
GISS Central Tropical Pacific (0–75 m; Conroy et al., 2014)				0.23		−7.82		0.88			
GISS Central Tropical Pacific (80–500 m; Conroy et al., 2014)				0.35		−11.83		0.83			
Central Tropical Pacific Line Island Ridge (0–75 m; Conroy et al., 2014)				0.31		−10.38		0.91			
Central Tropical Pacific Line Island Ridge (80–500 m; Conroy et al., 2014)				0.42		−14.38		0.94			
Western Central Pacific Kiritimati (0–1 m; Conroy et al., 2017)				0.17		−5.5		0.37			
Western Central Pacific Manus, Papua (0–1 m; Conroy et al., 2017)				0.20		−6.6		0.93			
East Equatorial Pacific Galapagos (0–1 m; Conroy et al., 2017)				0.08		−2.4		0.85			
Panama Bight (0–40 m; Benway & Mix, 2004)				0.25 and 0.14		−8.52 and −4.80		0.98 and 0.84			
Panama Bight (41–400 m; Benway & Mix, 2004)				0.47		−16.15		0.55			
Panama Bight (>400 m; Benway & Mix, 2004)				−1.89		65.42		0.95			
Deep Pacific/Indian (LeGrande & Schmidt, 2006)				−0.41		14.25		0.03			

Note. Regressions were performed for water masses with more than five data points. Significant relationships ($p \leq 0.05$) are indicated by bold font.

results rely on a small region and they are analyzed by each water mass. Further studies will be required for evaluating if the relationship between stable isotope and salinity could be extended for large areas as well as for understanding water mass processes.

For some SEP water masses the $\delta^{18}\text{O}$ values overlaps (Tables 3 and S5), which is clearly seen in the $\delta^{18}\text{O}$ -S relationships (Figure S13 in Supporting Information S1). In contrast, the δD -S relationship shows no overlapping in the δD values. Therefore, our results suggest that δD could be a promising tracer for water masses in the region. SAAW and ESSW are unique in that they exhibit statistically significant ($p < 0.05$) $\delta^{18}\text{O}$ -S and δD -S relationships. Both water masses feature a steep slope and low intercept (Figure S13 in Supporting Information S1; Table 4). Our results confirm previous work by LeGrande and Schmidt (2006) suggesting that SAAW is formed in the high southern latitudes (Table 4) and indicate the absence of sea-ice formation in the coastal region of the SEP (Figure S13). Indeed, the strong winds and low pressure system in the Subantarctic Zone bringing high rates of precipitation adding to the input of meltwater from Southern Patagonia are the principal mechanisms explaining the $\delta^{18}\text{O}$ -S and δD -S relationship for the SAAW.

The δD -S relationship for the ESSW follows the opposite trend expected for tropical regions (i.e., flat slopes and high intercepts). It is likely that the ESSW δD -S relationship is affected by vertical mixing (e.g., Conroy et al., 2014), causing the loss of its expected δD -S and $\delta^{18}O$ -S relationships typical for a tropical water mass (Figure S13; Table 4).

4.2.3. Non Conservative Water Mass Tracers and the Carbon Isotopic Composition ($\delta^{13}C_{DIC}$) of the Main SEP Water Masses

The spatial extent of available and new $\delta^{13}C_{DIC}$ data in the SEP allows us to expand the discussion of its $\delta^{13}C_{DIC}$ distribution, especially in the coastal section (Figures 4e–4f). SAAW, ESSW, AAIW, and PDW appear to be semi-conservative, maintaining $\delta^{13}C_{DIC}$ signatures from their source region (Figure 1d; Tables 2 and 3).

For STW, the mean $\delta^{13}C_{DIC}$ values in the coastal section are depleted compared to the oceanic section and the oceanic end-member (Figures S9 and S14; Tables 2 and 3). Nutrient contents (silicate, phosphate, and nitrate; Figures 2 and S3–S7; Table 3) and $\delta^{13}C_{air-sea}$ values are high in the coastal section compared with the oceanic sections (Figures S15 and S16; Table 3). Nitrate production is obvious in the STW in the coastal section (Figure 5f; Table 3) confirming previous studies that report that anaerobic anammox and/or denitrification processes are important in the upper part of the OMZ off Peru/Chile (Codispoti & Christensen, 1985; Hamersley et al., 2007; Llanillo et al., 2013; Thamdrup et al., 2006). We propose that depleted $\delta^{13}C_{DIC}$ and high $\delta^{13}C_{air-sea}$ values in the coastal section are related to vertical mixing of STW with $\delta^{13}C_{DIC}$ -depleted ESSW. The phosphate and nitrate concentration in the STW follow Redfield ratios (Figures 5b and 5e).

In contrast to the STW, SAAW exhibits high values of $\delta^{13}C_{DIC}$ with relative low $\delta^{13}C_{air-sea}$ in the coastal and oceanic sections (Figures S9 and S14–S16; Table 3) with high oxygen and low nutrient contents (silicate, phosphate, nitrate, and nitrite; Figures 2 and S3–S7; Table 3). The high $\delta^{13}C_{DIC}$ and oxygen content and low $\delta^{13}C_{air-sea}$ and nutrients values of SAAW reflect the high ventilation in the formation zone of the water mass. The silicate and phosphate content is slightly higher in the coastal than in the oceanic section (Figure 2; Table 3), reflecting additional nutrient input by river/fjords runoff (between 54° and 36°S) and upwelling of ESSW (between 38° and 32°S; Vargas et al., 2016 and 2018). A lack of nitrite confirms that redox processes within the SAAW are weaker compared with STW. We suggest that the slight excess in phosphate in the coastal region is sourced from the southern upwelling cells that exhibit relatively low values of $\delta^{13}C_{DIC}$ (Figure S12). In both oceanic and coastal sections, the phosphate and nitrate values of the SAAW follow the Redfield ratio (Figures 5b and 5e).

The subsurface ESSW show low $\delta^{13}C_{DIC}$ and oxygen values, with high nutrient contents (silicate, phosphate, nitrate, and nitrite; Figures 2, S3–S7, S9, and S14; Table 3) and $\delta^{13}C_{air-sea}$ in the coastal and oceanic sections (Figure S15; Table 3). These results may be explained by the accumulation of respired ^{12}C during the passage of the ESSW along the highly productive upwelling systems off western South America and in situ intense redox processes in the coastal section (Chavez & Messié, 2009; Daneri et al., 2000; Montero et al., 2007; Vergara et al., 2017). Close to the coast methanogenesis within suspended particles has been observed in the pycno/oxyclines (Holmes et al., 2000; Naqvi et al., 2010; Sansone et al., 2001; Troncoso et al., 2018), resulting in the accumulation of methane depleted $\delta^{13}C$ (Tenorio, 2021). This process may also be responsible for some of the highly depleted $\delta^{13}C_{DIC}$ values observed in ESSW. In the coastal section the phosphate and nitrate concentration in the ESSW diverge from Redfield ratios, in contrast to the oceanic section (Figures 5b and 5e), a feature previously reported to be typical for the SEP-OMZ (Llanillo et al., 2012; Silva et al., 2009). High nitrite contents are found in the ESSW reaching up to 7 $\mu\text{mol kg}^{-1}$ in the coastal section (Figures 5f and S6; Table 3). The presence of nitrite is best explained by the reduction of nitrate to nitrite via denitrification within the core of the OMZ (e.g., Farías et al., 2007; Graco et al., 2007; Llanillo et al., 2013; Silva et al., 2009).

The AAIW has high and similar $\delta^{13}C_{DIC}$ values along the coastal and oceanic sections. $\delta^{13}C_{air-sea}$ values are near to zero, similar to that of SAAW (Figures S14 and S15; Table 3). The AAIW exhibits relatively high values of oxygen and low nutrient content (as silicate, phosphate, nitrate, and nitrite; Figures 2 and S3–S7; Table 3). The phosphate and nitrate concentration in the AAIW is roughly aligned with redfield ratios in the oceanic and coastal section (Figures 5b and 5e) and a negligible nitrite production ($<0.4 \mu\text{mol kg}^{-1}$) is found (Figure 5f; Table 3). The similar $\delta^{13}C_{air-sea}$ values of AAIW and SAAW confirm that AAIW is well ventilated with a relatively young age, reinforcing previous work indicating that the SEP is the main formation region for AAIW (e.g., Bostock et al., 2010, 2013; Piola & Gordon, 1989). On its way north, the AAIW vanishes around 32°–30°S in the coastal section and at 24°S in the oceanic section. There is a progressive northward depletion in the AAIW $\delta^{13}C_{DIC}$ values

from +0.9‰ to +0.4‰ between 32° and 24°S (Martínez-Méndez et al., 2013a) due to mixing with ESSW/PDW in the lower part of the SEP-OMZ (Figure 4f).

The PDW has relatively low $\delta^{13}\text{C}_{\text{DIC}}$ values (Figures 4 and S14; Table 3) in the coastal and oceanic section. Oxygen levels are low and nutrient contents (as silicate, phosphate, and nitrate) are high (Figure 2; Table 3). The phosphate and nitrate concentrations in the PDW are aligned with the Redfield ratio in the oceanic and coastal sections (Figures 5b and 5e). Thus, the PDW is marked by a high content of respired ^{12}C (inferred from the high nutrient concentration) and is a poorly ventilated water mass. We do not include in the discussion the computed values for $\delta^{13}\text{C}_{\text{air-sea}}$ (Figures S15 and S16; Table 3) for the PDW. As explained above, it is a mixture of water masses with several sources and does not have any active exchange with the atmosphere.

In the coastal section the PDW/ESSW/AAIW mixing zone (Figure 4) exhibits relatively lower $\delta^{13}\text{C}_{\text{DIC}}$ values than in the oceanic section. This feature is not traceable with temperature, salinity, oxygen and phosphate, suggesting that depleted $\delta^{13}\text{C}_{\text{DIC}}$ from the OMZ/ESSW can reach deep waters and influence the distribution of this tracer in the coastal section (Silva et al., 2009; Vargas et al., 2021).

Between 200 and 1,800 m within ESPIW, AAIW, and PDW there are localized spots in the oceanic section that display very low $\delta^{13}\text{C}_{\text{DIC}}$ values (Figure 4), which may be caused by mesoscale eddies (Zhang et al., 2014). It has been observed that surface-to-deep eddies originating in the coastal section of the SEP can be advected far offshore into the oceanic section, contributing to long-distance biogeochemical transport affecting the characteristics of the water column (Czeschel et al., 2018). We suggest that such eddies possibly originate in the coastal zone transferring ESSW characteristics to intermediate and deep waters in the oceanic section of the study area.

In summary we find major differences in $\delta^{13}\text{C}_{\text{DIC}}$, nutrients, and oxygen content between the coastal and the oceanic section. We propose (a) the absence of the ESPIW in the coastal zone allowing the low oxygen, high nutrients, $\delta^{13}\text{C}_{\text{DIC}}$ depleted waters originating from the ESSW to extend much further south up to ~48°S there, while such waters are restricted to <30°S in the oceanic section, (b) the very different oxygen, nutrients, and $\delta^{13}\text{C}_{\text{DIC}}$ signatures of the STW along the two sections causing a significant depletion of $\delta^{13}\text{C}_{\text{DIC}}$ in the coastal section, and (c) the enhanced mixing of the upper-AAIW with ESSW resulting in lower average oxygen and $\delta^{13}\text{C}_{\text{DIC}}$ values in the coastal AAIW. These differences, especially in the upper ~1,000 m of the water column highlight the value of such coastal data for paleoceanographic reconstructions which are often based on sedimentary records from the continental margin.

4.2.4. Paleoceanographic Implications

Within the limitations described above, our new $\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}_{\text{DIC}}$, temperature, salinity, oxygen, and nutrient data combined with the percentage contribution per water mass (Figures 2–5 and S1–S9; Tables 2 and 3) can be used to differentiate modern water mass geometry (i.e., water mass distribution) in the SEP. This characterization improves our understanding of chemical processes within water masses, and can contribute to regional proxy calibrations.

Statistical analyses (i.e., Mann-Whitney tests) allow us to differentiate oxygen, hydrogen, and carbon stable isotopic values of the main water masses (Tables S5–S7). This considers mean isotopic values of each water mass and compares them to establish which water masses are isotopically correlated. We are aware that data for δD are still limited for the SEP, and patterns described here should be confirmed as further stable hydrogen isotope data become available. This is especially true for the PDW, which was excluded from Mann-Whitney analyses due to insufficient data. Thus, based on $\delta^{18}\text{O}$ and δD , SAAW/STW, SAAW/ESSW, and ESSW/AAIW can be differentiated, but not STW/ESSW, SAAW/AAIW, ESSW/PDW, and AAIW/PDW. While $\delta^{13}\text{C}_{\text{DIC}}$ can be used to differentiate between STW/ESSW (oceanic section), SAAW/ESSW, ESSW/AAIW, and AAIW/PDW, but not SAAW/STW and STW/ESSW (coastal section).

For reconstructions of past seawater salinities and temperatures, one important tracer is the oxygen isotopic composition of calcifiers, such as foraminifera. Hebbeln et al. (2000) and Mohtadi et al. (2005) studied the $\delta^{18}\text{O}_{\text{calcite}}$ in core-top planktonic foraminifera from a North-South latitudinal transect across the SEP, showing that foraminifera grown in the STW are relatively depleted compared to the ones from the SAAW. This suggests that planktonic foraminifera $\delta^{18}\text{O}_{\text{calcite}}$ is a possible route to study changes in the distribution of these surface waters in the past. Caniupán et al. (2011), Nürnberg et al. (2015), and Haddam et al. (2018) have subsequently used

planktonic foraminifera $\delta^{18}\text{O}_{\text{calcite}}$ to study changes in the spatial variations of oceanic fronts and surface water masses in the SEP.

It is important to note that the $\delta^{18}\text{O}_{\text{calcite}}$ composition of foraminifera is influenced by $\delta^{18}\text{O}_{\text{sw}}$ (closely coupled to salinity), temperature, vital and calcification effects, and ice volume (Bemis et al., 1998; Epstein et al., 1953; Lynch-Stieglitz et al., 1999; Marchitto et al., 2014; O'Neil et al., 1969; Shackleton, 1967; Urey, 1947). Temperature exerts a strong control on $\delta^{18}\text{O}_{\text{calcite}}$. Past temperature variations are commonly resolved by proxies, such as Mg/Ca ratios, or alkenones. $\delta^{18}\text{O}_{\text{calcite}}$ has uncertainties in the order of $>0.2\text{‰}$ that represent 1°C (Pearson, 2012). Over glacial-interglacial timescales global $\delta^{18}\text{O}_{\text{sw}}$ varies by $\sim 1.0\text{‰}$ – 1.2‰ (Fairbanks, 1989). Together, temperature and ice-volume related uncertainties result in a $\pm 0.4\text{‰}$ uncertainty in reconstructions of past $\delta^{18}\text{O}_{\text{sw}}$ values. This is very close to the range of SEP $\delta^{18}\text{O}_{\text{sw}}$ end-member values observed today. Within the SEP, the highest difference in $\delta^{18}\text{O}_{\text{sw}}$ end-member values (0.72‰) is observed between STW and SAAW (e.g., STW and ESSW = 0.29; SAAW and ESSW = 0.43; ESSW and AAIW = 0.31, ESSW and PDW = 0.21; AAIW and PDW = 0.01). Unless these uncertainties can be reduced, and/or past end-members become statistically different, it is unlikely that reconstructions of past $\delta^{18}\text{O}_{\text{sw}}$ values will provide statistically meaningful information about water mass distributions within the SEP.

The lack of local equations for describing the $\delta^{18}\text{O}$ -S relationship leads to additional uncertainties in paleosalinity reconstructions based on $\delta^{18}\text{O}_{\text{sw}}$ (Schmidt, 1999). In this regard, our results suggest that salinity inferences could be indeed implemented in the SEP, especially for SAAW and ESSW (Figure S13; Table 4), considering $\delta^{18}\text{O}$ -S and δD -S relationships documented here. Nevertheless, these regional paleosalinity reconstructions should rely on the assumption that such relationships remained unchanged over time. The use of the δD -S relationship either for salinity reconstructions or differentiation of water masses is a striking result, with deep implications for paleoceanographic reconstructions. Still, its potential must be explicitly revised as more stable hydrogen isotopic characterization of water masses in the SEP are conducted and validated.

The carbon isotopic composition of foraminifera ($\delta^{13}\text{C}_{\text{calcite}}$) from the fossil record is also often used for water mass reconstructions. The $\delta^{13}\text{C}_{\text{calcite}}$ in foraminifera is influenced by the ambient $\delta^{13}\text{C}_{\text{DIC}}$ and vital effects such as metabolic precipitation of calcium carbonate, respiration and symbiont photosynthesis (e.g., Ishimura et al., 2012; Mackensen et al., 1993; McCorkle & Keigwin, 1994; Spero, 1992; Spero et al., 2003). Some epifaunal benthic (living on top of sediments) have $\delta^{13}\text{C}_{\text{calcite}}$ that is similar (1–1 relationship) to bottom water $\delta^{13}\text{C}_{\text{DIC}}$ and can be used for reconstruct changes in ventilation and distribution of their habitat water masses (e.g., Schmitzner et al., 2017).

Martínez-Méndez et al. (2013a) and Haddam et al., (2020) used $\delta^{13}\text{C}_{\text{calcite}}$ in epifaunal foraminifera in sediment records from 27°S (970 kys) and 40° – 50°S (23 kys), respectively. Comparing epifaunal $\delta^{13}\text{C}_{\text{calcite}}$ with $\delta^{13}\text{C}_{\text{DIC}}$ values in situ (Martínez-Méndez et al., 2013a) and extrapolated from the oceanic region (Haddam et al., 2020) they reconstructed AAIW and PDW/CDW variability through time. The reconstructed $\delta^{13}\text{C}_{\text{calcite}}$ values in the sediment records are in a similar range as modern $\delta^{13}\text{C}_{\text{DIC}}$ values for AAIW and PDW.

Despite common strong vital effects, planktonic foraminifera $\delta^{13}\text{C}_{\text{calcite}}$ often indicate changes in surface to intermediate water masses geometry, ventilation, and productivity (e.g., Hebbeln et al., 2000; Mohtadi et al., 2008; Tapia et al., 2015, 2019). In the coastal section, the water masses show $\delta^{13}\text{C}_{\text{DIC}}$ end-member differences in a range of 2.29 and 0.52 (e.g., STW and SAAW = 1.39; STW and ESSW = 0.9; SAAW and ESSW = 2.29; ESSW and AAIW = 2, ESSW and PDW = 0.52; AAIW and PDW = 1.55). Thus, using epifaunal and planktonic foraminifera in the region could provide statistically meaningful information about changes in the characteristics of the water mass distributions within the coastal SEP.

$\delta^{13}\text{C}_{\text{calcite}}$ of planktonic foraminifera also may be used to reconstruct changes in surface waters within the SEP. Hebbeln et al. (2000) and Mohtadi et al. (2005) characterized the $\delta^{13}\text{C}_{\text{calcite}}$ of surface and subsurface planktonic foraminifera from core top samples recovered in a north-south transect in the coastal SEP. They found that surface planktonic foraminifera recorded low $\delta^{13}\text{C}_{\text{calcite}}$ beneath the STW compared to high $\delta^{13}\text{C}_{\text{calcite}}$ beneath the SAAW, corresponding to the regional productivity-upwelling patterns. These results are similar to $\delta^{13}\text{C}_{\text{DIC}}$ values of the surface waters indicating that planktonic foraminifera $\delta^{13}\text{C}$ in the region can be used as a proxy for surface water $\delta^{13}\text{C}_{\text{DIC}}$.

In terms of using $\delta^{18}\text{O}_{\text{calcite}}$, in combination with temperature reconstructions, to calculate $\delta^{18}\text{O}_{\text{sw}}$, to trace water masses it may be useful to compare this with $\delta^{13}\text{C}_{\text{calcite}}$, in a multi-proxy approach. Hebbeln et al. (2000) plotted for the first time $\delta^{18}\text{O}_{\text{calcite}}$ versus $\delta^{13}\text{C}_{\text{calcite}}$ in planktonic foraminifera for the SEP, showing a regional relationship that can be used for reconstructing the geometry of surface water masses. Our results show that $\delta^{18}\text{O}$ or δD and $\delta^{13}\text{C}_{\text{DIC}}$ relationships in sea water can be used as a modern analog for water mass geometry reconstructions (by time slices) in the region from surface to deep (Figures 5i and 5j).

Most paleoceanographic reconstructions for the SEP from the late Quaternary are based on sediment cores collected from the continental margin. During the last decades, these records were generally compared with open ocean data, because data from nearer to the coast was lacking (e.g., Castillo et al., 2017; De Pol-Holz et al., 2006, 2007; Haddam et al., 2018, 2020; Siani et al., 2013). Our new compilation of $\delta^{13}\text{C}_{\text{DIC}}$ data combined with temperature, salinity, oxygen, and nutrient data (Figures 2 and 4) reveal significant differences in the distribution of water masses in the upper $\sim 1,000$ m of the water column between the oceanic and the coastal sections. Our data furthermore expose a general absence of the ESPIW (subducted SAAW) in the coastal section (Figures 2–4). This puts some caveats on interpretations of previous studies (e.g., De Pol-Holz et al., 2006, 2007 and Castillo et al., 2017) that considered ESPIW as the main water mass that ventilates the upper part of the coastal ESSW/SEP-OMZ. Instead we argue that in the coastal section SAAW and AAIW might play a similar role as open ocean ESPIW, in ventilating the upper ESSW.

5. Conclusions

We present the first spatial characterization of $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ along with temperature, salinity, oxygen, and nutrient contents of the main water masses in the SEP in an oceanic and a coastal section. Our analysis reproduces the well-known oceanic distribution of the main SEP water masses, originating in the equatorial, subtropical and subantarctic Pacific regions and it is the first one to include a highly resolved EOMP analysis of AAIW and PDW in the coastal SEP. However, our data also reveal that the water column structure in the coastal section clearly deviates from its oceanic counterpart, especially due to the absence of the ESPIW in the coastal section.

For past oceanographic reconstructions on marine sediment, we can use $\delta^{18}\text{O}$ and δD to differentiate between SAAW/STW, SAAW/ESSW, and ESSW/AAIW, but not between STW/ESSW, SAAW/AAIW, ESSW/PDW, and AAIW/PDW. $\delta^{18}\text{O}$ -S and δD -S relationships are statistically significant for the SAAW and ESSW, suggesting that the SAAW have an origin in high-latitudes with strong influences of high precipitation and melted-ice from the Patagonian Ice Sheet. Our study confirms that ESSW follows an opposite trend expected for tropical regions, possibly due to advection and mixing processes with surface waters. $\delta^{13}\text{C}_{\text{DIC}}$ can be used as a proxy to differentiate between STW/ESSW (oceanic section), SAAW/ESSW, ESSW/AAIW, and AAIW/PDW, but not between SAAW/STW and STW/ESSW (coastal section). The $\delta^{13}\text{C}_{\text{DIC}}$, oxygen, and nutrients database for the oceanic section has a good spatial cover and can be compared with the new coastal data set, highlighting strong differences in water mass geometry above 1,000 m water depth in the SEP. In the coastal section, (a) the surface waters fill a smaller depth range, (b) the ESPIW (subducted SAAW) is absent allowing ESSW to spread much further south, (c) the STW $\delta^{13}\text{C}_{\text{DIC}}$ signature differs considerably from its oceanic counterpart, (d) the upper-AAIW with ESSW resulting in lower average oxygen and $\delta^{13}\text{C}_{\text{DIC}}$ values in the coastal AAIW, and (e) the PDW/ESSW/AAIW mixing zone shows lower $\delta^{13}\text{C}_{\text{DIC}}$ values than in the oceanic section. All these differences result in on average lower $\delta^{13}\text{C}_{\text{DIC}}$ values in the coastal section that partly deviate by $>1\%$ from the comparable depth/latitude setting in the oceanic section. These deviations clearly point out that it is necessary to compare paleoceanographic records recovered from intermediate waters along the western South American continental margin with present-day hydrological analogs from the coastal section.

The relationships of $\delta^{18}\text{O}$, δD , and $\delta^{13}\text{C}_{\text{DIC}}$ with each other and with other parameters like temperature and oxygen offer a multiproxy database that can be used as present-day hydrological analogs for reconstructions of past water mass distributions. In addition, using the relationship of planktonic and epifaunal benthic foraminifera $\delta^{18}\text{O}_{\text{calcite}}$ versus $\delta^{13}\text{C}_{\text{calcite}}$ in specific time slices may enable the characterization of past SEP water column geometries from surface to deep waters.

Data Availability Statement

All seawater hydrological and stable isotope data used here are provided in the supplementary materials and have been submitted to PANGAEA (<https://www.pangaea.de/>), GLODAP (<https://www.glodap.info/>) and NASA/GISS Global Seawater Oxygen Isotope Data Base (<https://data.giss.nasa.gov/o18data/>).

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