1	Influence of post-Tehuano oceanographic processes in the dynamics of the
2	CO ₂ system in the Gulf of Tehuantepec, Mexico
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36 Key Points

1. The aragonite saturation horizon is close to the surface near the coast.

38 2. Reported air-sea CO₂ fluxes are the largest observed to date in the Mexican
39 Pacific.

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41 Abstract

This investigation reports, for the first time, results of CO₂ system variables in the Gulf of 42 43 Tehuantepec, located in the Mexican tropical Pacific. We quantified the post-Tehuano 44 concentration of dissolved inorganic carbon (DIC) and pH (April 2013). These values were used to calculate pCO₂, aragonite saturation (Ω_{Ar}) and air-sea CO₂ fluxes (FCO₂). The 45 46 intense vertical stratification was found to contribute to the biogeochemical processes in 47 surface waters (< 70 m). However, in post-Tehuano conditions, high pCO₂ (~1000 µatm) and DIC concentrations (2200 μ mol kg⁻¹), as well as low Ω_{Ar} (~1.1) and pH (~7.5) remain 48 49 in surface waters for a few days after Tehuano winds have weakened. We identified four 50 oceanographic areas: a) a highly mixed region due to previous Tehuano events; b) coastal 51 upwelling in the western region; c) mesoscale eddies; and d) a poleward surface coastal 52 current. The first three promoted the influence of Subtropical Subsurface Water in the 53 chemistry of surface waters, whereas the coastal current contributed to the horizontal advection of DIC. The calculated CO₂ fluxes ranged from -2.3 mmol m⁻² d⁻¹ in areas 54 with stratified waters, to over 25 mmol $m^{-2} d^{-1}$ for mixed areas. Positive values indicate an 55 ocean-to-atmosphere flux. Our findings suggest that the Gulf of Tehuantepec is a major 56 57 source of CO_2 into the atmosphere.

59IndexTerms:Eastern TropicalPacific,OceanAcidification,60Tehuano gap winds, carbonate system, mesoscale structures, carbon fluxes.

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62 1 Introduction

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Approximately 50% of the CO₂ that is absorbed in the subtropical region of the Pacific Ocean returns to the atmosphere in the tropics [*Feely et al.*, 1997; *Ishii et al.*, 2014]. Variations in the concentration of dissolved inorganic carbon and air-sea CO₂ fluxes in the tropical ocean are both enhanced by high CO₂ levels in subsurface water. These, in turn, are regulated by dynamic processes derived from wind forcing, such as coastal upwelling events, thermal fronts and mesoscale eddies, among others [*Chen et al.*, 2007; *Friederich et al.*, 2008; *Wang et al.*, 2006].

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In the Gulf of Tehuantepec (GoT), intermittent northerly winds, called "nortes" or 72 "Tehuanos" (speed above 10 m s⁻¹) result from pressure gradients between the Gulf of 73 74 Mexico and the GoT from November to March [Barton et al., 1993; Trasviña et al., 75 1995]. These winds produce strong changes in the structure of the water column and a 76 complex coastal circulation. Under the influence of Tehuanos, surface water flows offshore, 77 which causes mixing and entrainment of subsurface water. The result is a temperature drop of up to 8 °C at the center of the GoT, and the formation of a cold water plume that may 78 79 stretch over 400 km offshore and be more than 200 km wide [Barton et al., 1993; Trasviña 80 et al., 1995].

Wind relaxation after Tehuanos results in the formation of mesoscale structures [*Barton et al.*, 2009; *Chang et al.*, 2012]. The most frequent structure is an anticyclonic eddy at the

GoT western region [*Barton et al.*, 2009; *Willett et al.*, 2006], which can last several months. Also reported is the presence of a cyclonic eddy in the eastern/central GoT, as well as a coastal current to the east that travels north/northwest parallel to the coast [*Barton et al.*, 2009; *Velázquez-Muñoz et al.*, 2011]. Once the Tehuano season is over, during May-June [*Romero-Centeno et al.*, 2007] the GoT becomes highly stratified, displaying a strong pycnocline [*Fiedler et al.*, 2013], mesoscale structures, and coastal-trapped waves related to baroclinic instabilities [*Flores-Vidal et al.*, 2014].

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91 The importance of mesoscale structures lies in their effect on the vertical distribution of 92 chemical properties, particulate inorganic and organic matter, heat, mass, and living 93 organisms and their transport offshore [Adams and Flierl, 2010; Chierici et al., 2005; 94 Samuelsen and O'Brien, 2008]. Anticyclonic eddies, for example, deepen the pycnocline by 95 Ekman pumping, and therefore keep subsurface waters that are DIC-rich, with low pH and 96 near-undersaturated aragonite levels, away from the surface. The opposite is true when 97 cyclonic eddies occur and eddy-induced upwelling transports subsurface waters toward the 98 surface.

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In the Gulf of Tehuantepec, water masses in the upper 500 m are composed primarily of Tropical Surface Water (TSW) and Subtropical Subsurface Water (StSsW) [*Barton et al.*, 2009; *Fiedler and Talley*, 2006]. StSsW (Table 1) contains part of the oxygen minimum layer (OML) and the maximum dissolved inorganic carbon (>2200 μ mol kg⁻¹) [*Franco et al.*, 2014]. The upper depth limit of this water mass ranges between 70 and 100 m; therefore, it could have a significant influence on the biogeochemical processes in GoT surface waters when mesoscale structures, heavy mixing, or upwelling occur. For this region of the Pacific Ocean, the depth distribution of these water masses has been reported
to depend, to a greater or lesser extent, on seasonal variations of the oceanic circulation
[*Godínez et al.*, 2010].

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111 Due to the presence of intense north winds, few in-situ oceanographic studies have been 112 conducted in this region. Hence, current knowledge on carbon biogeochemistry in the GoT 113 is scarce. To date, there are no published studies on the CO₂ system in this region. The 114 Tehuano and post-Tehuano conditions are expected to lead to an increase in DIC 115 concentrations and a decrease in pH of surface water accordingly. Furthermore, the 116 magnitude of air-sea fluxes of CO₂ in the region remains unknown. Based on studies of 117 other tropical regions in the Eastern Tropical Pacific (ETP), the Gulf of Tehuantepec is 118 expected to be a source of CO₂ to the atmosphere [Franco et al., 2014; Paulmier et al., 119 2008].

120 Ecologically important coral species such as Pocillopora damicornis, P. meandrina and 121 Porites Panamensis live in the coastal areas of the GoT [López-Pérez et al., 2014]. 122 Aragonite saturation state variability may affect corals and other calcifying species such as 123 coccolithophorids and foraminifera [Müller et al., 2010; Rixen et al., 2012]. However, no 124 published information is available on the carbon chemistry conditions in which calcifying 125 organisms live. The present study provides the first quantitative information on the CO_2 126 system in the Gulf of Tehuantepec. The oceanographic and biogeochemical data collected 127 under post-Tehuano conditions show the effects of oceanographic conditions on the vertical 128 distribution of carbon variables across the water column that impact surface carbon fluxes 129 and the depth of the aragonite saturation horizon. Due to the strong variability in oceanic

and atmospheric conditions, the GoT might be considered as a natural laboratory forinvestigating the CO₂ system.

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133 2 Methods

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135 2.1 Sample and data collection

Sampling was carried out during an oceanographic cruise led by the Mexican Navy (Secretaría de Marina) aboard RV *Altair* (Figure 1). Data on temperature, conductivity and pressure were recorded to a maximum depth of 500 m at 26 stations using a factorycalibrated Seabird SBE19 CTD. From these data, salinity (PS-78) and density (EOS-80) were calculated.

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At each station (Figure 1), water was collected at nine depths using 5 L Niskin bottles attached to a hydrographic wire. Sampling depth was calculated from the cable length, using a cable counter, and the line angle, using an inclinometer). Water samples were stored in 500 mL sodium borosilicate bottles and preserved with 100 μ L of HgCl₂ saturated solution. Afterwards, bottles were sealed with ApiezonTM grease to prevent evaporation and contact with the atmosphere.

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The concentration of dissolved inorganic carbon (DIC) was measured using the coulometric method described by *Johnson et al.* [1987]. Certified reference material (CRM) from Dr. Andrew Dickson's laboratory at Scripps Institution of Oceanography, University of California, San Diego, was used for assessing the precision and accuracy of 153 measurements. The reference material gave a relative difference averaging $2.2 \pm 1.1 \mu mol$ 154 kg⁻¹, with a maximum of 4 $\mu mol kg^{-1}$ (0.2% error) with respect to the certified value.

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156 The pH was measured using a glass electrode with an Orion potentiometer at 25 °C. The 157 electrode slope was calculated 24 hours before the analysis using NBS buffers of pH 7.01 158 and 4.01; afterwards, the electrode was kept immersed in filtered seawater. The reference 159 material mentioned above was used as a seawater pH standard. The pH value in the 160 seawater scale from the certified reference material was calculated with the 161 CO2SYS program using the certified DIC and TA values [Lewis and Wallace, 162 1998]. The millivoltage of the reference material was recorded at the beginning and end of 163 each session. All measurements were performed at 25 °C in the seawater scale (pHsw).

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165 The aragonite saturation state (Ω_{Ar}), pH_{sw}, and pCO₂ at in-situ temperature, salinity and 166 pressure were calculated with the CO2SYS program [Lewis and Wallace, 1998] adapted for 167 Matlab by Van Heuven et al. [2009], using discrete DIC and pH_{sw} measurements (25 °C). 168 The dissociation constants proposed by *Lueker et al.* [2000] were used for this purpose. 169 This resulted in a precision of \pm 0.04 units for pH_{sw} in situ, \pm 0.2 units for Ω_{Ar} and \pm 170 56 μ atm for pCO₂. The uncertainty for pCO₂ is higher than what would be obtained with the TA-DIC combination; however, the pCO₂ range of variability observed was 28 times 171 172 greater than the error, and hence our measurements are representative of the processes 173 taking place in the GoT.

174 The air-sea CO₂ flux (FCO₂) (mmol C $m^{-2} d^{-1}$) was calculated as:

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 $FCO_2 = kK_o(pCO_{2w} - pCO_{2a}) \tag{1}$

177 where k is the gas transfer velocity, which is a function of wind speed, calculated according to [Wanninkhof, 1992]; the coefficients used were 0.31 and 0.39 for weak (<6 ms⁻¹) and 178 strong (>6 ms⁻¹) wind speeds, respectively; K_0 is the aqueous-phase solubility of CO₂ in 179 180 seawater at in situ temperature and salinity, calculated using the equations of *Weiss* [1974]; pCO_{2w} and pCO_{2a} are the CO₂ partial pressure in water and air, respectively. This 181 182 calculation used the average atmospheric pCO₂ of 398.35 µatm reported for April 2013 by the Mauna Loa observatory (ftp://aftp.cmdl.noaa.gov/). Wind speed data (m s⁻¹) were 183 184 obtained from daily NOAA SeaWinds satellite images with a spatial resolution of 0.25 degrees [*Zhang et al.*, 2006a; *Zhang et al.*, 2006b]. The calculated error for FCO₂ was ± 0.5 185 mmol m⁻² d⁻¹ for winds ≤ 2.5 m s⁻¹ (this condition prevailed throughout the sampling 186 campaign), with a peak of 1.3 mmol $m^{-2} d^{-1}$ for high-speed winds (4 m s⁻¹). 187

188 The stratification was calculated with the method of Simpson and Bowers [1981] for the 189 upper 300 m. Wind data were obtained from daily composite NOAA SeaWinds satellite 190 images (www.ncdc.noaa.gov) with a spatial resolution of 0.25 degrees. Wind stress was calculated according to Large and Pond [1981]. Mesoscale eddies were identified visually 191 192 using satellite images of the sea level anomaly (SSHa) 193 (http://www.aviso.oceanobs.com/duacs/). These data consist of interpolated daily images 194 resulting from multi-satellite (2 to 4 satellites) observations of 10- to 30-day cycles for the 195 same period of hydrographic observations, and with the same spatial resolution as wind 196 data. Geostrophic speed and dynamic height were calculated using a no-motion reference 197 level of 300 dbar. This level adequately represents the surface circulation and was applied 198 by *Barton et al.* [2009] and *Flores-Vidal et al.* [2014] for the same region.

200 **3 Results**

201 **3.1** Water masses

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203 In line with previous studies for this region [Barton et al., 2009; Fiedler and Talley, 204 2006], the water masses observed in the first 500 m depth were the TSW and StSsW 205 (Figure 2). TSW is distributed mainly from the surface layer down to the 18°C isotherm, 206 where the StSsW starts (Figure 2a). In this layer, TSW showed low DIC concentrations (1923-2050 µmol kg⁻¹) and low pCO₂ values (276-648 µatm, not shown) compared with 207 208 subsurface water (Figure 2c). StSsW showed higher DIC concentrations, ranging between 209 2200 and >2270 µmol kg-1 (Figure 2c). The depth of the upper boundary of the DIC-rich 210 StSsW water mass varies throughout the study area as a reflection of the dominant physical 211 processes in each region. In regions dominated by anticyclonic eddies, StSsW was observed 212 at approximately 100 m depth, whereas in regions of cyclonic circulation it occurred at less 213 than 30 m. In areas with the highest vertical mixing resulting from previous Tehuano 214 events, this water was found near the surface (Figure 2a). Consequently, the rise and/or 215 upwelling of StSsW is expected to enrich surface water with DIC. This process is described 216 below in terms of the physical dynamics that take place after an intense north wind event.

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218 **3.2 Post-Tehuano conditions**

Prior to the sampling period, five wind events with speed greater than 10 m s⁻¹ occurred between March and the first week of April 2013; the most intense reached 19.8 m s⁻¹ during the first week of March (Figure 3a). These exerted a strong wind stress on the sea surface (Figure 3b) and declined gradually to post-Tehuano conditions (Figure 3c). During the April sampling under post-Tehuano conditions, winds fluctuated between ~ 2 and 5 m s⁻¹ 224 and caused a minor forcing (Figure 3c), which nonetheless was of sufficient intensity to 225 produce coastal upwelling areas in the eastern and western ends of the GoT (Figure 3c). The combination of strong winds and subsequent calm led to different oceanographic 226 227 conditions: the coastal region displayed a highly mixed zone and another area 228 with upwelling; mesoscale eddies and a poleward coastal current were also identified. Accordingly, the distribution patterns of CO₂ variables were directly associated with the 229 various oceanographic conditions. Each of these conditions and their effect on the 230 231 chemistry of the CO₂ system are described below.

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233 3.2.1 Coastal upwelling

Westerly winds (~0.03–0.04 N m²) flowing parallel to the GoT west coast were recorded 234 235 during the sampling campaign (six days), (Figure 3c). These caused an Ekman transport of 75–96 m³ s⁻¹ 100 m⁻¹ (calculated as per *Schwing et al.* [1996] for the average stress over the 236 237 six days) and a rise of isopycnals in the first 60 km from the coast (transects I and II, 238 Figures 4-Ia and IIa), with an ascension of water from 60 m up to 20–30 m, as noted in 239 figures. The water flowed with the highest geostrophic speed observed in all the study area (53 cm s⁻¹, Figure 4-Ib). The importance of this finding lies in that previous studies have 240 241 focused only on the effect of processes directly derived from intense Tehuano winds, 242 omitting information related to the fact that upwelling events are also formed in this region. Coastal upwelling events promote an ascent of subsurface water, leading to changes in DIC 243 concentrations, pH values and Ω_{Ar} , and may cause significant changes in the air-sea flux 244 of CO2. At 30 m depth near the coast (6-20 km), DIC levels of 2150 µmol kg⁻¹ were 245 recorded, as well as 2224 µmol kg⁻¹ in transects I and II, respectively (Figures 4-Ic and 4-246

IIc). High DIC concentrations were due to a greater influence of StSsW. Minimum pH and Ω_{Ar} values (Figure 4-IId-e) were observed just 6 km off the coast at depths where peak DIC concentrations were recorded. Similar to the above variables, the aragonite saturation horizon ($\Omega_{Ar} = 1$) rose 100 m in just 100 km, reaching a depth of 28 meters near the coast (Figure 4-Ie and 4-IIe). Moreover, pCO₂ values increased to levels as high as 1900 µatm (Figure 4-If).

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- 254 **3.2.2** Area of intense vertical mixing
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256 An area of intense vertical mixing was detected in the central region of the Gulf of 257 Tehuantepec. Although wind stress was relatively low during sampling, five strong wind events in the previous days recorded mean wind stress values of ~ 0.15 N m⁻² (Figure 3b). 258 Vertical mixing and reduced stratification (634 J m⁻³) resulting from these wind events 259 260 were detected during the sampling conducted two weeks later. The fact that the upper StSsW limit (Figure 2) is represented by the 25.5 kg m⁻³ isopycnal suggests that this DIC-261 262 rich water mass was closer to the surface. The stations near the coast showed the highest 263 subsurface DIC concentrations and lower pH, 2218 µmol kg^{-1} and ~7.7, 264 respectively (Figure 4-III), along with pCO₂ values of 1750 µatm (Figure 4-IIIf). Besides, just 80 km off the coast, the aragonite saturation horizon was observed 160 m 265 266 above the depth where it occurs 120 km offshore (190 m).

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268 **3.2.3 Mesoscale eddies**

270 Two anticyclonic eddies were recorded: one in the Gulf of Tehuantepec (A1) and another to 271 the east of it (A2) (Figure 5). The sequence of daily altimetry images between March and 272 April (not shown) suggests these structures resulted from Tehuano and Papagayo winds, 273 respectively. Likewise, altimetry data pointed to the presence of two cyclonic eddies 274 localized in the GoT at the beginning of the sampling period. Only the central cyclonic 275 eddy was observed during the sampling period (C1). As detailed below, anticyclonic 276 eddies promoted the sinking of the aragonite saturation horizon and the pH, pCO₂, and DIC 277 isolines; the opposite occurred in association with cyclonic eddies.

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279 The cyclonic eddy in the center of the GoT (C1) was adjacent to the coast and stretched 280 down to 300 m, as evidenced by the temperature distribution in section III of Figure 4. 281 Within this cyclonic eddy, DIC-rich water ranged from 20 down to 200 m. Similarly, pH 282 values were 7.7 and 8.1 at the bottom and surface, respectively. Aragonite saturation and 283 pCO₂ fluctuated from 0.9 to 4.2, and from 1752 to 289 µatm, respectively, following the 284 same variation pattern as DIC. In the eastern portion of the cyclonic eddy (Figure 4, 285 transect IV.), sampled on April 14-15 when it occupied most of the GoT, more pronounced 286 isotherm slopes were observed, particularly near the coast. This resulted in a better 287 definition of cyclonic circulation, with currents flowing to the west (poleward) near the 288 coast and to the east (equatorward) from 100 km offshore. The depth of isotherms 289 (isopycnals) was minimal at the center of the eddy. Consequently, a higher DIC 290 concentration relative to the coastline and offshore was observed. Along the coastline, the 291 DIC-rich StSsW carried waters of relatively low pH (~7.6), and a shallower saturation 292 horizon (~30 m) was evident close to the coast. These values show that this eddy caused a 293 slight rise of StSsW, with the consequent DIC enrichment.

295 On the eastern edge of the Tehuantepec anticyclonic eddy measured during the cruise, isotherms and isopycnals sank down to 50 m, with a current of \sim 30 cm s⁻¹ (Figure 4, 296 297 sections I a-f and II a-f, stations located away from the coast). This led to the sinking of the aragonite saturation horizon and isolines of pH 7.6 and DIC 2200 µmol kg⁻¹, which were 298 >80 meters deeper than in the more coastal station, with peak values of pH and Ω_{Ar} in the 299 eddy region (Figure 4, section I d-e). Furthermore, pCO₂ values ranged between 400 and 300 301 1180 µatm between 100 and 120 km off the coast, and the aragonite saturation horizon was 302 found between 120 and 200 m depth. The accumulation of surface water within the anticyclonic eddy facilitated the stratification of the water column (1418 J m⁻³), this being 303 304 the maximum value recorded for the study area.

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The influence of the Papagayo eddy was evident in section V. The depth of the thermocline increased in the three stations farther away from the coast compared to the rest of the transect, while it occurred at a depth of only 10 m near the coast. DIC-rich water (2200 μ mol kg⁻¹, pH 7.6) was located at ~70 m depth at the station closest to the center of this eddy (Figure 4 section V, oceanic stations).

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The changes observed in the CO_2 system resulting from mesoscale eddies suggest that these structures may have a significant effect on biogeochemical and ecological processes in the region. Mesoscale eddies occur throughout the year, being more frequent during the Tehuano season [*Willett et al.*, 2006]; hence, their effects on the CO_2 system could be apparent throughout the year.

318 **3.2.4 Coastal current**

319 The data obtained in transects I-V, as well as the maps of geostrophic velocity derived from altimetry, reveal a poleward coastal flow (4.4 cm s⁻¹). Temporal coverage of data used 320 321 in this study is not enough to discern whether this flow is a constant current or derives from 322 eddy rims associated mainly with cyclonic eddies (Figure 4). Previous studies refer to a 323 poleward coastal current detected at the same region during winter, spring and summer 324 [Barton et al., 2009; Flores-Vidal et al., 2011; Trasviña and Barton, 2008; Willett et al., 325 2006] ;[Velázquez-Muñoz et al., 2011]. Furthermore, geostrophic velocity in section I 326 (Figure 4) indicates a poleward subsurface flow in spite of the coastal upwelling and the 327 anticyclonic eddy. Therefore, we assume the poleward flow observed in this study is the 328 same structure reported in the literature. The core of this current was between the 100 and 329 180 m, i.e. StSsW. Given its characteristics, this current was associated with a higher DIC 330 concentration, lower pH and lower Ω_{Ar} , and was more corrosive than water from the same depth collected offshore, except for sections IV and V, where the DIC concentration near 331 332 the coast was similar to or higher than in the rest of the water column.

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334 3.2.5 Surface distribution

The surface distribution of the variables studied reflects the effect of the oceanographic conditions described in the previous sections (mixing, upwelling, eddies, coastal current). σ - θ shows the surface maxima near the coast in the highly mixed region (Figure 6a, 16°45' N, 96° W) associated with the cyclonic circulation that promotes the rise of subsurface water and the redistribution of mixed water, leading to CO₂ enrichment. In contrast, regions 340 dominated by anticyclonic circulation showed a deepening of low-density isopycnals 341 (Figure 6). Surface DIC concentrations, directly related to waters of lower density, ranged between 1923 and 2218 µmol kg⁻¹ (Figure 6b), coupled with a higher pH (Figure 6c); these 342 were located at 14°30'–15° N and 97°–97°30' W, (Figure 6b). Separately, Ω_{Ar} of the upper 343 344 layer (not shown) ranged between 1.1 and 4.3. Peaks were associated with the most 345 stratified region, and minimum levels were recorded in the region with the highest mixing 346 and upwelling. The 20 m depth was dominated by a highly mixed region (15°30' N, 95°45' W) and the dome of the central cyclonic eddy (C1, Figures 5 and 6) (15°15' N, 96°30' W, 347 Figure 6d), with DIC >2200 μ mol kg⁻¹ and low pH (Figure 5e, f); minimum values were 348 349 observed in the area most affected by the Tehuantepec anticyclonic eddy (A1).

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- 351 3.2.6 Air-sea flux of CO₂
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353 The increase in DIC concentration in surface waters translated into high calculated fluxes of CO_2 into the atmosphere (Figure 7), which ranged between -2.3 and 42 mmol C 354 $m^{-2} d^{-1}$. Peak values were observed in the highly mixed area (42 mmol C $m^{-2} d^{-1}$), whereas a 355 flux of 5 mmol C $m^{-2} d^{-1}$ was estimated in the coastal upwelling region. Separately, the 356 regions under the influence of anticyclonic eddies displayed a flux indicating near-357 358 equilibrium with the atmosphere. The rest of the region dominated by cyclonic circulation displayed low fluxes into the ocean of -2.6 mmol C $m^{-2} d^{-1}$. The intense air-359 360 sea fluxes in the mixed area which resulted from previous wind and upwelling events 361 confirm that the GoT may be a source of CO₂ into the atmosphere during the entrainment of 362 subsurface waters, due to the turbulent mixing driven by the wind. The results shown represent what remains after the last Tehuano event ended, and wind speeds fell below 5 m s⁻¹. Such high fluxes are driven by a strong air-sea DIC gradient and these post-Tehuano DIC fluxes may remain for several days after a strong wind event. Air- sea fluxes may be larger during Tehuano events when wind stress breaks the interface and increases gas exchange. Considering that the Tehuano wind season lasts approximately four months, the Gulf of Tehuantepec represents an important source of CO_2 in the Eastern Tropical Pacific, likely being the most important area reported so far for the Mexican Pacific.

- 370
- 371 4 Discussion
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373 This paper describes the development of post-Tehuano conditions during April 2013 and 374 the consequent spatial variation in the CO₂ system. The greatest wind forcing occurs during 375 the Tehuanos season from November to March [*Trasviña et al.*, 1995]. However, April can be considered as a transitional month, a post-Tehuano condition where the wind drops 376 to $\sim 3-5$ m s⁻¹. Four oceanographic conditions were identified in the Tehuantepec region 377 378 during the post-Tehuano period: 1) a highly mixed coastal region; 2) mesoscale eddies; 3) a 379 coastal upwelling in the western region; and 4) a coastal current (Figure 8). This section 380 discusses how these conditions impacted the CO₂ system, as well as their importance and 381 ecological implications.

382 4.1.1 Vertical mixing

The water column near the coast and in the center of the study area (Figure 4, coastal stations in transects III and IV) showed the greatest impact of wind during previous Tehuano events. The highest surface DIC and pCO₂ concentrations, together with the 386 greatest flux of CO₂ into the atmosphere and minimum surface pH and Ω_{Ar} are expected 387 under this scenario According to Trasviña et al. [1995], vertical mixing is the process that 388 leads to the greater thermal anomalies after Tehuano events, since the mixed layer expands 389 almost immediately after the onset of a strong wind event. Flores-Vidal et al. [2014] show 390 in their figure 6 that water at 60 to 70 m depth can be transported to the surface as a result 391 of a strong wind. When the wind weakens, the region with the lowest vertical stratification 392 is confined to the coast, near the head of the gulf. In this work, the mixed area is evidenced by the 54% reduction of stratification (784 J m⁻³) compared to the maximum 393 stratification within the Tehuantepec anticyclonic eddy (1414 Jm⁻³), typical of the tropical 394 395 region [Fiedler et al., 2013].

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In this region, surface DIC concentrations exceeded 2200 μ mol kg⁻¹ and pCO₂ levels were 397 398 above 1600 µatm. These figures show higher values than those recorded in other regions of 399 the North Eastern Tropical Pacific (NETP) influenced by StSsW (1290-1340 µatm [Franco et al., 2014]), similar to the coastal region from Colima to Michoacan, and slightly lower 400 401 than DIC concentrations reported for the Midriff Islands region in the Gulf of California (~2270 µmol kg⁻¹) [*Hernandez-Ayon et al.*, 2013]. Although the whole NETP tends to be 402 403 highly stratified at the surface with an underlying StSsW, the difference between the GoT 404 and other areas of the Mexican Pacific lies in that Tehuano events break the stratification 405 and promote the vertical mixing and the rise of DIC-rich subsurface water (SSW), hence allowing waters with high DIC and pCO2 concentrations reach the surface. This area 406 showed minimum pH and Ω_{Ar} values; pH and decreased 0.6 units, while Ω_{Ar} dropped 2.6 407 units (68%), when compared with the surface peaks observed in the region of anticyclonic 408

eddies. The minimum surface Ω_{Ar} (1.2) was lower than figures reported for other regions of the Eastern Tropical Pacific, such as Papagayo (~2.0–3.2) [*Rixen et al.*, 2012] and the NETP (3.3–4.1) [*Franco et al.*, 2013]. Consequently, the saturation horizon in this region of the GoT is located at only 30 m depth, thus making of it the shallowest horizon reported for the Mexican Tropical Pacific (70–100 m), similar to data reported for upwelling regions off California [*Feely et al.*, 2008; *Franco et al.*, 2014].

415 4.1.2 Coastal upwelling

416 Upwelling areas observed in the coasts of transects I and II resulted in an enrichment 417 of DIC and pCO₂, and a drop in pH and Ω_{Ar} in surface water near the coast (section 3.2.1). 418 The intensity of the upwelling is similar to that observed in Baja California upwelling 419 zones [Koračin et al., 2004; Perez-Brunius et al., 2007], since the wind flowing parallel to the coast (~5 m s⁻¹) produces a wind stress of ~0.04 Nm^2 and an Ekman transport of 75–96 420 m³ s⁻¹ 100m⁻¹. Coastal upwelling can have a significant impact not only on the coast but 421 422 also at the mesoscale level, since according to Trasviña et al. [1995], the Tehuantepec 423 anticyclonic eddies are fed by water from the west, i.e. the region where upwelled water is 424 located during coastal upwelling. In their study, Müller-Karger and Fuentes-Yaco 425 [2000] reported positive chlorophyll anomalies within anticyclonic eddies, which were 426 attributed to the effect of Tehuano events. However, these anomalies may also be due to the 427 entrance of nutrient-rich waters from upwelling events on the west coast.

428

429 Near the coast, DIC and pCO₂ values were higher than the values predicted to occur by 430 year 2100 for the global ocean [*Hoegh-Guldberg et al.*, 2014]. Surface pH and Ω_{Ar} were 431 similar to those reported for other upwelling regions such as Papagayo, Costa Rica (7.86– 7.92) [*Rixen et al.*, 2012], and the upwelling filament off the western African
coast (pH_{Tot}=7.94–8.05) [*Loucaides et al.*, 2012]. The depth of the saturation horizon in the
upwelling zone was minimal (41 m); this horizon was deeper than the one reported for Pt.
St. George, California, but shallower than in the Baja California coast [*Feely et al.*, 2008].
From the above, it is clear that upwelling produces a marked variability in the CO₂ system
under post-Tehuano conditions, similar to important upwelling regions elsewhere.

438

439 4.1.3 Mesoscale eddies

440

The key factors that determine the degree of influence of mesoscale eddies on the water 441 442 column and its chemical properties are their residence time, intensity and direction of 443 rotation [*Willett et al.*, 2006]. In the present study, the anticyclonic eddy (A1) was the 444 largest eddy observed in Tehuantepec and the first to appear after the first Tehuano event 445 (Figures 3–4). According to the literature this is always the case, in addition to having a 446 longer duration than cyclonic eddies [Clarke, 1988; McCreary et al., 1989; Trasviña et al., 447 1995]. This means that changes in the CO_2 system are evident shortly after the wind forcing 448 and remain over the lifetime of cyclonic eddies. Consistent with observations of *Barton et* 449 al. [1993], this anticyclonic eddy was intensified by subsequent winds after its formation; 450 in addition, it reached a size similar to that of other anticyclonic eddies that are typical of 451 this area [Palacios and Bograd, 2005; Willett et al., 2006]. Vertically, its effect in the water 452 column is related to the sinking of isotherms down to 180 m. Although only the outer 453 region of the eddy could be described through sampling, its center is likely deeper.

455 In the Gulf of Tehuantepec, the sinking of the thermocline (and, consequently, of the 456 upper StSsW) by anticyclonic eddies contributed to surface water with minimum DIC and pCO₂ levels (pH and Ω_{Ar} maxima). This effect has been observed in other areas, such as the 457 458 Haida anticyclonic eddy close to the Queen Charlotte Island, Canada, where the DIC 459 concentration was lower within the cyclonic eddy than in the surrounding water [Chierici et 460 al., 2005]. Therefore, it is clear that low DIC concentrations lead the acid-base 461 chemistry towards higher pH and Ω_{Ar} levels. Additionally, the accumulation of warm water 462 promotes a stronger stratification, which further limits the exchange of DIC between 463 subsurface and surface waters [Franco et al., 2014]. As a result, the above conditions 464 produce a mixed layer with a carbon chemistry characterized by two potential scenarios: 1) 465 waters with DIC and pH close to equilibrium with the atmosphere, when waters are 466 oligotrophic; or 2) waters with slightly high pH coupled with DIC below equilibrium 467 levels, when photosynthesis processes have occurred within the eddy.

468

469 Although the limited exchange with subsurface water lowers the input of nutrients and 470 affects primary productivity, it is possible to find positive chlorophyll anomalies in 471 anticyclonic eddies in the GoT [Müller-Karger and Fuentes-Yaco, 2000]. In this case, 472 primary production within the anticyclonic eddy might even turn it into a CO₂ sink, similar 473 to the Haida eddy during 2001, which was reported as a CO₂ sink relative to the 474 surrounding water [Chierici et al., 2005]. Considering that Tehuantepec anticyclonic eddies 475 have a lifetime of up to 6 months and can travel up to 2000 km to the west [Palacios and 476 Bograd, 2005; Willett et al., 2006], these structures may be functioning as carbon sinks 477 with low DIC concentrations and high pH values if they contain phytoplankton biomass.

478 Also, this type of eddies promotes a deeper aragonite saturation horizon, hence providing a479 suitable habitat for calcifying organisms such as foraminifera and coccolithophores.

480

481 The Papagayo anticyclonic eddy (A2) This eddy catalyzed the disappearance of the 482 second cyclonic eddy by increasing the dynamic height and sinking the subsurface water, 483 which led to a drop in DIC and an increase in both pH and Ω_{Ar} . Based on numerical 484 simulations [Velazquez-Muñoz et al. [2014], Papagayo eddies seem to influence circulation 485 patterns within the GoT. However, this fact is documented for the first time through in situ 486 data that suggest a complex interaction between the GoT and Central America. This 487 connectivity could be an important source of exchange of chemical properties, similar to 488 the way in which Tehuantepec cyclonic eddies export mass, heat, chemicals and organisms 489 out of the continental shelf.

490

491 On the other hand, the cyclonic circulation covered a large part of the GoT; however, the 492 cyclonic eddy was formed one month after the anticyclonic one, when the latter drifted 493 away from the coast (Figure 3). The eastern eddy lasted one week and disappeared once 494 the Papagayo eddy started approaching as it travelled westward. The fact that this type of 495 structure requires more time to form and is weaker and ephemeral could explain why 496 cyclonic eddies were not always detected in previous studies [Velázquez-Muñoz et al., 497 2011]. Consequently, their physical importance and biogeochemistry have been little 498 studied; only their relevance on primary productivity has been addressed in previous 499 investigations [Gonzalez-Silvera et al. [2004].

501 The present study revealed that the cyclonic eddy produced shallower pycno- and 502 thermocline, and maintained conditions that promote DIC enrichment near the surface. 503 Surface DIC levels within the eddy exceeded those found within eddies near the Canary Islands (2095 µmol kg⁻¹) [González-Dávila et al., 2006]. This is due to the Tehuantepec 504 505 cyclonic eddy being deeper and the rise of isotherms being greater relative to conditions in 506 the Canary Islands (100 m); besides, subsurface water in that region contains lower DIC 507 concentrations ($\leq 2155 \,\mu$ mol) compared to StSsW. In contrast, compared to the Opal eddy 508 in Hawaii, characterized by a stronger vertical pumping (~120 m) [*Chen et al.*, 2008], our 509 data show similar DIC concentrations in surface waters within the eddy, but higher in the 510 rest of the water column. These differences are due to a lower DIC content in the water 511 masses across their study region. This underlines the importance of the type of water mass and its origin in the study of both the carbon chemistry and its global balance. In our 512 513 case, the pumping of DIC-rich, low-pH water (StSsW) contributes to maintain in surface 514 water the enrichment conditions resulting from previous mixing. These dynamic and 515 chemical conditions make of the Gulf of Tehuantepec a DIC-rich region as well as a source 516 of carbon into the atmosphere.

517

The pumping of water toward the surface within cyclonic eddies increases nutrient inputs and fosters primary productivity [*Bibby et al.*, 2008; *Chen et al.*, 2008; *González-Dávila et al.*, 2006]. For the region studied here, other investigations have reported that the nutricline may be at a depth between 6 and 32 m [*Lara-Lara and Bazán-Guzmán* [2005], hence increasing productivity. However, while eddies increase nutrient levels and DIC fosters primary production, causing cyclonic eddies to function as "production islands", the shallow saturation horizon impacts CaCO₃ precipitation rates and might
negatively affect calcifying organisms.

526 Based on the above discussion, the effects of mesoscale eddies on carbonate chemistry 527 are similar to those reported for other regions of the world. The distinctive feature in the 528 Mexican Tropical Pacific is that mesoscale eddies can account for up to 50% of the total variability of sea surface height [Godinez et al., 2010] in the absence of inter-annual El 529 530 Niño/La Niña conditions, and occur in a region where subsurface DIC levels are high. This 531 fosters a greater vertical transport of DIC toward the surface when cyclonic eddies occur. In 532 the particular case of Tehuantepec this effect could be more significant, given that 533 mesoscale eddies are formed year-round [Barton et al., 2009; Trasviña and Barton, 2008; 534 *Willett et al.*, 2006]. The recurrent presence of eddies implies a constant pumping of carbon 535 to the surface in the case of cyclonic eddies, or to deeper waters in the case of anticyclonic 536 eddies. This highlights their importance in modulating the seasonal variability of the CO_2 537 system in coastal ecosystems across the region.

538

539 4.1.4 Poleward coastal current

540

Another mesoscale structure of importance in relation to carbon chemistry in the GoT is the coastal current that flows to the northwest. Although this has been reported previously as a surface current by other authors [*Barton et al.*, 2009; *Flores-Vidal et al.*, 2011; *Machain-Castillo et al.*, 2008; *Velázquez-Muñoz et al.*, 2011], in the present study it occurred as a surface current to the east and a subsurface one to the west. This current functions as a DIC advection mechanism. DIC concentrations are similar across all the 547 coastal stations at the depth where this current is located, and differ from levels observed in 548 all other stations (except for transect IV). The current runs through the mixed area and 549 transports DIC-rich water to coastal regions located west of the study area, thereby 550 contributing to high DIC concentrations and low pH and Ω_{Ar} levels. Therefore, this coastal 551 current contributes to the role of this region as a source of CO₂ into 552 the atmosphere. However, further in-depth studies are needed on this current to better 553 understand its mechanisms and importance on the variability of the CO₂ system.

554

555 4.2 Air-sea flux of CO₂

556

557 The positive carbon flux values (FCO₂) calculated for post-Tehuano conditions indicate that the system functions as a source of CO₂ into the atmosphere. The present study reports 558 the highest fluxes recorded to date for the Mexican Pacific, (42 mmol $m^2 d^{-1}$), and the 559 560 second highest for the Eastern Tropical Pacific above its oxygen-minimum zone after the upwelling in the Peruvian coasts, for which fluxes around 51 mmol C $m^{-2} d^{-1}$ have been 561 562 reported [Friederich et al., 2008]. Our values are also higher than those reported for other tropical regions of Mexico ($\leq 3.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ north of our study area) and the coast of 563 Chile $(0.8 - 25 \text{ mmol m}^{-2} \text{ d}^{-1})$ [*Franco et al.*, 2014; *Paulmier et al.*, 2008]. 564

565

Although CO_2 fluxes are high under post-Tehuano conditions and were observed in a small area, it is reasonable to expect that the flux of CO_2 during Tehuano conditions is even higher and comprises a greater area. Compared with other regions, the gulf of Tehuantepec contributes significantly to the carbon balance in Mexico and should be included in carbon 570 inventories. In general, the significant CO₂ fluxes observed were due to the high carbon 571 content in the zone mixed either by Tehuano winds or by the upwelling of surface waters 572 associated with StSsW. In this geographic region, stratification limits carbon exchange 573 [Franco et al., 2014], while mixing produces the opposite effect, carrying DIC-enriched 574 water toward the surface. On the other hand, the shallower the upper limit of StSsW, the 575 greater the flux of CO₂ [Franco et al., 2014]. The processes that carried this water mass 576 closer to the surface were upwelling, followed by cyclonic eddies, both of which fostered a rise in DIC in surface water and, hence, the flux of CO₂ into the atmosphere. In 577 578 contrast, anticyclonic eddies caused the sinking of this water mass, leading to CO₂ fluxes 579 close to the equilibrium.

Observations made in the Mexican Tropical Pacific by *Franco et al.* [2014] revealed that the ocean behaves as a weak source of CO_2 (3.3 mmol m⁻² d⁻¹) when the influence of StSsW on surface water is weak, and as a carbon sink when TSW promotes stratification. In that region, the processes regulating the influence of StSsW and DIC concentrations were advection and high stratification (~1400 J m⁻³). As shown in Figure 8, in addition to these processes, vertical mixing, coastal upwelling and the Ekman pumping in cyclonic eddies can influence the flux of CO_2 into the atmosphere in the Gulf of Tehuantepec.

587

In addition to the forcing by physical processes, biological activity regulates the intensity and variability of carbon fluxes in surface water [*Wang et al.*, 2006]. This work did not estimate the effect of biological activity on the CO₂ system in the GoT. However, the extent of the biological contribution in the study area may be significant, since primary productivity increases significantly after the Tehuano forcing [*Gonzalez-Silvera et al.*, 2004]. As estimated by *Wang et al.* [2006] through a biogeochemical model 594 coupled with oceanic circulation, primary productivity removes 0.87 Pg C per year across 595 the equatorial Pacific, i.e. 59% of the carbon contributed by physical processes to surface 596 water (1.47 Pg C). The April transitional period showed positive fluxes, suggesting that the 597 GoT is a source of CO₂ into the atmosphere. Since during the post-Tehuano conditions the 598 Gulf of Tehuantepec shows a residual flux of lesser intensity in terms of mixing and 599 entrainment compared with the Tehuano season. In fact, if the same DIC concentrations as those reported here were considered to be under high wind conditions (20 m s⁻¹) the result 600 would be larger. Given the maximum fluxes reported in this study (42 mmol $m^{-2} d^{-1}$), it can 601 602 be considered that this region remains as a source of CO₂ into the atmosphere for four months approximately (~120 d), producing approximately 61 g C m⁻². If we consider 603 604 that the Tehuano season produces a plume of cold water measuring some 400 x 200 km 605 [Barton et al., 1993], a contribution of up to 4.9 Tg C could be estimated in the plume 606 region alone. This accounts for $\sim 0.8\%$ of the annual flux of CO₂ for the whole Equatorial 607 Pacific, estimated at 0.6 Pg C [*Wang et al.*, 2006]. The increase of phytoplankton biomass 608 after Tehuano events would also increase DIC demand, which in turn would affect FCO₂. 609 Assuming biological DIC removal holds the same rate as in the Equatorial Pacific, primary 610 productivity could remove as much as 2.9 Tg C, making the process more biologically-611 mediated, compared to conditions during a Tehuano event. However, it is important to keep 612 in mind that the extent of such effect will depend on initial DIC concentrations, intensity of 613 the physical forcing, redistribution by anticyclonic eddies, and time elapsed between the 614 initial enrichment and the subsequent biological response.

- 615
- 616 4.3 Ecological implications
- 617

618 The increase in DIC concentrations near the surface during post-Tehuano conditions and 619 the consequent decrease in pH and Ω_{Ar} have important implications for coastal ecosystems in the region. Low pH and Ω_{Ar} levels may be associated with negative effects on the 620 621 growth, calcification rates, or survival of various species of organisms. However, the 622 particular effects and their magnitude depend on each individual species, and also vary with 623 the stage of the life cycle and the duration of exposure [Price et al., 2011; Tambutté et al., 624 2011]. Along with other species, the coral *Pocillopora damicornis* prospers in the GoT and 625 is regarded as the most abundant coral species in the region [López-Pérez et al., 2014]. It has been reported that pH values of 7.4 and Ω_{Ar} levels of 1.1, such as those found in this 626 627 work, produce an over-regulation of genes encoding for the proteins involved in 628 calcification, while a pH of 7.2 (RR = 0.68) decreases their regulation [*Vidal-Dupiol et al.*, 629 2013]. This may explain why this coral displays a higher calcification rate in regions with 630 no upwelling events, compared with upwelling zones such as those in Panama and the 631 Galápagos Islands [Manzello, 2010]. The calcification rate of Pocillopora meandrina has 632 been observed to decrease by 50% when exposed to water with an aragonite saturation state of 2.0 [Muehllehner and Edmunds, 2008]. In this investigation, more than 50% of the 633 634 stations studied (19 out of 26) showed Ω_{Ar} values lower than 2.0 in the first 30 m. In the 635 present investigation, pH and Ω_{Ar} values of 7.7 and 1.4, respectively, were recorded in the 636 center of the cyclonic eddy at depths less than 27 m (Figure 9a and b). Similar values 637 (pH=7.7, Ω_{Ar} =) were recorded at 10 m depth, at the station nearest to the coastline, 6 km 638 off Puerto Angel, Oax. Although there are no records about the variability of the carbonate 639 system on the coral reefs inside the GoT, temperature data from *Glynn and Morales* [1997] 640 suggest Tehuano events have a direct effect on the coastal oceanography of the region, and 641 therefore corals are being exposed to DIC-rich water with StSsW content. Glynn and 642 *Morales* [1997] registered a 4°C decrease in seawater temperature (from ~24 to ~20°C) at the reef base (8 m depth) in La Entrega coral reef, Huatulco, Oaxaca, during a six-day 643 survey on February 1996, right after two Tehuano events of 17 and 15 m s⁻¹ took place in 644 645 the GOT (February 12-14 and 17), as registered on Seawinds satellite data [Zhang et al., 646 2006b]. According to *Barton et al.* [2009], who carried out an oceanographic sampling 647 campaign at the GoT around the same time (February 10-27, 1996), the cold water plume 648 was located near the coast of Huatulco, where surface temperatures were 25°C. These 649 autors observed that the cold water plume produced in the central GoT is generally 650 displaced westward during wind relaxation and therefore may approach the coast of 651 Huatulco. The vertical distribution of water properties near Huatulco showed the ascencion 652 of StSsW near the coast as a response to wind-forcing. Based on our findings, it is considered that these and similar species are being exposed to water with Ω_{Ar} that is 653 suboptimal for their development. Further coastal records regarding pH and Ω_{Ar} variability 654 655 are needed to confirm this finding.

656

According to <u>López-Pérez et al. [2014]</u>, only 14 of the 34 coral species living in the Mexican Pacific [<u>Reves-Bonilla et al., 2010</u>] are distributed along the coast of Oaxaca. Furthermore, <u>López-Pérez and Hernández-Ballesteros [2004</u>] report that coral populations in Huatulco, Oaxaca, are a mixture of patches under various recovery stages. Preliminary results from an ongoing investigation indicate that, among the coral species living in the area, *Porites panamensis* displays the lowest growth, density, and calcification rates in the Mexican Pacific. These figures are 50% lower in our study area [A. Lopez-Perez, 664 unpublished data, 2015] than the minimum values registered in Marietas Islands in the 665 central region of the Mexican Pacific where the StSsW is also present, albeit with a lesser 666 contact with the surface [Franco et al., 2014; Norzagarav-López et al., 2013]. In turn, 667 corals of P. panamensis living in the Marietas Islands region display lower growth and 668 calcification rates relative to those in Baja California. In Puerto Angel, Oaxaca, this species 669 is extremely rare and prospers only in the upper three meters of depth [Norzagaray-López et al., 2013; Reves-Bonilla and Levte-Morales, 1998]. The low pH and Ω_{Ar} may be 670 negatively affecting the abundance, distribution, and calcification rate of corals. However, 671 672 the coastal zone displays high variability and is also influenced by other processes (river 673 inputs, eutrophication, waves, etc.) that modulate the degree of exposure of corals to 674 corrosive water.

675 Other calcifying organisms in the GoT, such as foraminifera and coccolitophores, may also be exposed to low pH values. According to Machain-Castillo et al. [2008], shells of 676 677 recent planktonic foraminifera in GoT sediments show differences in assemblages, 678 depeding on the location of the wind jet, with Globigerina bulloides being the most 679 abundant species (21%). Shell dissolution rates were higher near the coast (15.5 - 16.5 N 680 and 95 - 95.5 W), at the same location of the highly mixed area in our study. Nitrate 681 concentations in the overlying water column (21 µM at 50 m depth) confirmed the 682 influence of subsurface water (1 - 21 μ M). However, for a wide range of inter- and intra-specific responses to $[CO_3^{-2}]$ variability [*Aldridge et al.*, 2012], as their 683 684 calcification intensity and dissolution rate respond to different environmental drivers and calcification strategies [de Nooijer et al., 2009]. Previous studies indicate that along with 685 $[CO_3^{-2}]$ availability, ortophosphate levels also affect calcification and promote dissolution. 686

687 The relative contribution of the different environmental drivers is unknown for most 688 foraminifera species. *Globigerina bulloides* from the North Atlantic Ocean showed a 689 positive correlation between size-normalized weight (SNW, an indicator of calcification in for a for a minifera) and $[CO_3^{-2}]$, but the negative correlation of SNW with ortophospate and 690 691 nitrate was higher [Aldridge et al., 2012]. Benthic foraminifera from hydrothermal vents in 692 the Gulf of Baja California and Ischia Island, Italy, showed shifts and impoverishment of 693 assemblages, as well as an increased post-mortem dissolution at pH values of 7.5 - 7.8, 694 which supassed the minima found in our study [*Dias et al.*, 2010; *Pettit et al.*, 2013]. These 695 changes may affect for a in the long term, as reported by Moy et al. [2009], who 696 found that modern shells of G. bulloides are 30–35% lighter than those from the Holocene. 697 Coccolitophorides display a similar response, with some species being more suceptible to 698 test dissolution than others. According to Müller et al. [2010], Emiliana huxlei and 699 Coccolithus braarudii displayed a 9% and 29% drop in growth rate, respectively, when 700 exposed to water with pCO₂ values of 1150 and 930 µatm, respectively. In our study such pCO₂ values were observed near the coast at the first 30 m depth. In addition, some species 701 702 of both foraminifera and coccolitophorids have developed metabolic strategies to cope with 703 variations in pH and [CO₃₋₂] [de Nooijer et al., 2009; Taylor et al., 2011], i.e. increasing cell pH to favor the formation and precipitation of $[CO_3^{-2}]$ at the expense of other metabolic 704 705 functions. Therefore, we would expect these calcifying groups to be affected by the 706 variability of the carbon system inside the GoT; however, exposure studies with local 707 species are needed to confirm and quantify this effect.

708

The presence of coral reefs and other calcifiers in the region raises several questions: how do they survive in such conditions? Is exposure to water sufficiently 711 extensive/intense to cause negative effects? Have organisms living in the GoT developed 712 adaptative strategies to withstand these conditions? If they have indeed adapted, this 713 region could serve as a window into the future under an ocean acidification scenario, since 714 many of the pH values reported here are lower than those predicted to occur in tropical 715 regions by year 2100 (7.7). Furthermore, the GoT may act as a positive feedback to climate 716 change; according to *Ishii et al.* [2014], half of the carbon that enters the Pacific ocean in 717 the extratropics is released back to the atmosphore at the tropics. This implies that under a 718 climate change scenario, the increase in anthropogenic carbon would result in a larger DIC 719 enrichement of the StSsW. On the other hand, the rising sea surface temperature decreases 720 CO₂ solubility and enhances stratification of the water column, mantaining DIC-rich 721 conditions under the thermocline, until Tehuano events disrupt the water column and 722 promote DIC to surface and return to the atmosphere, increasing FCO₂. These conditions will further decrease pH and Ω_{Ar} . However, as the water column is already enriched with 723 724 DIC, the change rate may be lower than in temperate regions. To understand these 725 processes, further studies are needed, focusing on the variability of the carbonate system in 726 the GoT at different spatial and temporal scales, as well as studies on the exposure of 727 various GoT native organisms to these conditions, in order to deepen our understanding of 728 how pH and Ω_{Ar} influence coral reef-building species and other calcifying organisms that 729 inhabit Gulf of Tehuantepec coastal ecosystems.

730

731 **5** Conclusions

733 This investigation analyzed the post-Tehuano oceanographic conditions in the Gulf of 734 Tehuantepec and their effect on the CO₂ system. The main oceanographic structures 735 observed were areas of high mixing near the head of the gulf, areas with coastal upwelling, 736 mesoscale eddies, and a coastal current flowing to the west; all of these co-occurred during 737 April 2013. This complex set of structures produced significant changes in the chemistry of 738 dissolved inorganic carbon (DIC). The highly mixed region showed the highest surface 739 DIC concentrations and pCO₂ values, high air-sea CO₂ fluxes, and minimum surface pH 740 and aragonite saturation levels. These values exceed those predicted for the global ocean in 741 year 2100, and are among the most extreme conditions reported for the Mexican Pacific. 742 Coastal upwelling and the cyclonic eddy led to the lifting of isolines of high DIC 743 concentration (low pH and Ω_{Ar}) corresponding to StSsW close to the surface. By 744 contrast, anticyclonic eddies caused the sinking of the StSsW, which is the main source of 745 DIC in the region. The coastal current transported water toward the west, redistributing 746 previously mixed water; this led to the advection of DIC to the west of the study area.

747

The estimated carbon fluxes are the highest reported for the Mexican Pacific and rank second across the Tropical Eastern Pacific, even when determined under post-Tehuano conditions. The findings reported in this paper suggest that the study region is a major source of CO_2 into the atmosphere and should be included in carbon inventories. Our results highlight the importance of regions whose dynamics is dominated by winds jets in the global carbon balance.

754

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- 1104 FIGURE LIST
- 1105
- Figure 1. Study area. Blue symbols represent the sampling grid in the Gulf of Tehuantepec.Oceanographic sections are indicated in Roman numbers I to V.
- 1107

Figure 2. T-S diagrams for the cruise carried out April 13-18, 2013. (a) All T-S data. Dark red color indicates data of 200 dbar and over. (b) Selected profiles located at the mesoscale eddies, for the anticyclonic eddy (red) cyclonic eddy (blue), and the area most affected by the wind adjacent to the coast (magenta). (c) T-S-DIC plot for discrete samples (0-200 m of depth). TSW: Tropical Surface Water. StSsW: Subtropical Subsurface Water.

1114

1115 Figure 3. Wind conditions previous and during the sampling campaign. a) Wind velocity (m

- 1116 s^{-1}) from March 1 to April 19[,] 2013 at 15.5°N and 95°W. The green shaded area indicates
- 1117 the sampling period. b) Mean wind stress $(N m^{-2})$ during Tehuano winds between March 1
- and April 11, 2013. c) Mean post-Tehuano wind stress (N m⁻²) between April 12 and 18,
- 1119 2013. Note the different color scales used for strong and weak winds.
- 1120

1121 Figure 4. Vertical distribution of properties within the upper 200 m for sections I-V. (a)

- 1122 Line contours are σ_{θ} (kg m⁻³) while colors indicate temperature (°C). Black triangles in (a)
- 1123 specify the location of CTD casts. (b) Geostrophic velocity (m s^{-1}) relative to 300 dbar.
- 1124 Positive velocities represent poleward (westward) currents, (c) dissolved inorganic carbon
- 1125 (μ mol kg⁻¹), (d) *in situ* pH_{*sw*} (e) Ω Ar and (f) pCO₂ (μ atm). The aragonite saturation horizon
- 1126 ($\Omega_{Ar}=1$) is shown as a black contour. The red, green, blue and purple bars at the top of the
- figure indicate the stations most influenced by anticyclonic eddies, coastal upwelling,
- 1128 cyclonic eddies, and vertical mixing, respectively.
- 1129

Figure 5. Altimetry Sea surface height anomaly (cm) and associated geostrophic currents 1130 (m s⁻¹), showing the evolution of eddies at the Gulf of Tehuantepec and its vicinity, 1131 1132 Previous to Tehuano events (March 1), right after the four Tehuano events (March 29) and during the sampling campaign (April 13-19, 2013). C1= Tehuantepec cyclonic eddy. 1133 1134 A1=Tehuantepec anticyclonic eddy. A2= Papagayo anticyclonic eddy. The sampling cruise 1135 grid is shown magenta in April 13 and 18 panel. in 1136 (http://www.aviso.oceanobs.com/duacs/).

1137

1138Figure 6. Distribution of water sample measurements obtained during April, 2013 at surface1139(left) and 20 m deep (right). σ_{θ} (kg m⁻³) (a, d), (b, e) dissolved inorganic carbon (µmol kg⁻¹), and (c, f) *in situ* pH_{sw}. C1= cyclonic eddy. A1= anticyclonic eddy. A2= anticyclonic1141flow. Arrows indicate eddy location.

- 1143 Figure 7. Air-Sea CO₂ flux (mmol C m⁻² d⁻¹) in the Gulf of Tehuantepec during April 13-
- 1144 18, 2013. The white contour indicates the flux threshold of zero mmol C m⁻² d⁻¹. Positive
- values indicate fluxes toward the atmosphere.
- 1146
- 1147 Figure 8. Processes involved in the variability of the CO₂ system at the Gulf of
- 1148 Tehuantepec during Post-Tehuano conditions. Red and blue colors indicate CO₂ sources
- and sinks and respectively.
- 1150
- 1151 Figure 9. Coverage of water with inorganic carbon chemistry attributes below the optimum
- 1152 for coral calcifiers. Zonal variation of a) DIC concentration, b) pH, and c) Ω_{Ar} values at the
- 1153 outermost stations. The x axis describes distance from west to east. d) Depth of the 2200
- 1154 μ mol kg⁻¹ DIC contour line and e) that of $\Omega_{Ar} \le 1.4$, f) Location of the stations shown in (a)
- 1155 to (c).
- 1156

- Table 1. Surface and subsurface water masses identified at the study area and their chemical properties. 1159

	Water mass	
	Tropical Surface Water (TSW)	Subtropical Subsurface Water (StSsW)
Temperature	T >25°C	9≤T≤18°C
Salinity	S<34.9, Higher salinity values during Mar-May.	34.5≤S≤35.0
Geographic range	5°N - 15°N, Isotherm 25	From South Pacific to 23°N
Vertical range	0~50 m.	70-500 m
Origin	Eastern Tropical Pacific	South Pacific gyre
DIC concentration	1906±29 μmol kg ⁻¹	2252-2268 μmol kg ⁻¹
pCO ₂	560±260 µatm	1290-1340 µatm
Dissolved Oxygen	>150 µmol kg ⁻¹	<30
References	[Cepeda-Morales et al., 2013;	[Cepeda-Morales et al., 2013; Franco,
	Fiedler, 1992; Fiedler and Talley,	2011; O'Connor et al., 2002]
	2006; Franco et al., 2014; Wyrtki,	
	<u>1967</u>]iedler y Talley, 2006;	
	Cepeda-Morales <i>et al.</i> , 2013;	
	Franco <i>et al.</i> , 2014)	



















