1	New insights of fCO <sub>2</sub> variability in the tropical eastern Pacific Ocean using
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- 50 Abstract
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52 Complex oceanic circulation and air-sea interaction make the eastern tropical Pacific Ocean 53 (ETPO) a highly variable source of  $CO_2$  to the atmosphere. Although the scientific community have 55 amassed 70,000 surface fugacities of carbon dioxide (fCO<sub>2</sub>) datapoints within the ETPO region 56 over the past 25 years, the spatial and temporal resolution of this dataset is insufficient to fully 57 quantify the seasonal to inter-annual variability of the region, a region where fCO<sub>2</sub> has been 58 observed to fluctuate by >300 µatm.

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60 Upwelling and rainfall events dominate the surface physical and chemical characteristics of 61 the ETPO, with both yielding unique signatures in sea surface temperature and salinity. Thus, we 62 explore the potential of using a statistical description of fCO2 within sea-surface salinity-63 temperature space. These SSS/SST relationships are based on in-situ SOCAT data collected within 64 the ETPO. This statistical description is then applied to high resolution (0.25°) SMOS sea surface 65 salinity and OSTIA sea surface temperature in order to compute regional fCO<sub>2</sub>. As a result, we are 66 able to resolve fCO<sub>2</sub> at sufficiently high resolution to elucidate the influence various physical 67 processes have on the  $fCO_2$  of the surface ETPO.

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69 Normalised (to 2014) oceanic fCO<sub>2</sub> between July 2010 and June 2014 within the entire ETPO was 39 (+/-10.7) µatm supersaturated with respect to 2014 atmospheric partial pressures, and 70 featured a CO<sub>2</sub> outgassing of 1.51 (+/- 0.41) mmol m<sup>-2</sup> d<sup>-1</sup>. Values of fCO<sub>2</sub> within the ETPO were 71 72 found to be broadly split between southeast and a northwest regions. The north west, central and 73 offshore regions were supersaturated, with wintertime wind jet driven upwelling found to be the first order control on fCO2 values. This contrasts with the southeastern/ Gulf of Panama region, 74 75 where heavy rainfall combined with rapid stratification of the upper water-column act to dilute 76 dissolved inorganic carbon, and yield fCO<sub>2</sub> values undersaturated with respect to atmospheric 77 fugacities of CO<sub>2</sub>.

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#### 1. Introduction

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90 Perturbations to the global carbon cycle caused by anthropogenically driven increases in 91 atmospheric partial pressures of  $CO_2$  (p $CO_2$ ) produce an acute requirement to understand interreservoir carbon fluxes (Le Quéré et al 2014). However, assessing these fluxes, especially the flux 92 93 between the atmosphere and surface ocean is challenging, as pCO<sub>2</sub> within the oceanic reservoir 94 varies considerably both spatially and temporally. Fortunately, considerable effort has been made in 95 recording oceanic pCO<sub>2</sub> (or fugacity-  $fCO_2$ ) over the past 50 years, with roughly 10 million 96 individual measurements of global surface ocean pCO2 taken, processed, flagged and assembled 97 into two large datasets: the surface ocean CO<sub>2</sub> atlas (SOCAT) and Lamont-Doherty Earth 98 Observatory (LDEO) carbon dioxide database (Bakker et al., 2014; Takahashi et al., 2014). Both 99 databases make heavy use of 'vessel of opportunity' derived pCO<sub>2</sub> data, resulting in a 100 heterogeneous dataset with the majority of measurements collected within the tight confines of 101 commercial shipping lanes. 102 103 The first stage in efforts to estimate large scale air sea fluxes requires the extrapolation of these

104 discrete surface pCO<sub>2</sub> observations over large areas of surface ocean. Completing a basic 105 extrapolation of this vessel of opportunity based data results in a spatially-patchy pCO<sub>2</sub> field, as 106 seen in the one degree gridded product available from SOCAT (Bakker et al., 2014). Therefore, in 107 order to achieve improved spatial coverage, a frequently used solution is to fit data-driven 108 diagnostic models (e.g. Feely et al. 2006; Park et al. 2010; Rödenbeck et al., 2013). These models 109 use observed correlations between physical properties and the pCO<sub>2</sub> observed under these 110 conditions. In addition, statistical criteria based on the surface ocean observations (for example, 111 satellite imagery) and/ or neural networks have been used to identify biogeochemical provinces in 112 order to improve the accuracy of the extrapolated field (Boutin et al. 1999; Cosca et al. 2003; 113 Rangama et al., 2005; Landschützer et al., 2014). Although the quality of these extrapolation 114 methods have been refined over the past few years, in part due to the increasing number of in situ 115 measurements, the interannual variability of the global air-sea CO<sub>2</sub> flux obtained using different 116 data-driven methods still substantially differ, and further work is required to unify our estimates and 117 improve understanding of this air-sea flux.

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The recent (2010-present) availability of sea surface salinity from the Soil Moisture Ocean

Salinity (SMOS) mission has provided a new tool in statistically modelled pCO<sub>2</sub> studies, as now the relationship between surface temperature, salinity, density and pCO<sub>2</sub> can be utilised in high resolution statistical descriptions of pCO<sub>2</sub> within TS space. It is this relationship that is explored within this paper in order to quantify inter and intra annual variability within the oceanographically complex eastern tropical Pacific Ocean (ETPO) region between 4 °N and 18 °N, and east of 95 °W (Fig. 1).

The ETPO region is influenced by northern and southern hemisphere trade winds, the 126 127 doldrums, strong seasonal wind jets, heavy rainfall, strong solar heating and the El Nino-Southern 128 Oscillation (ENSO), (Kessler, 2006). Within the ETPO the Intertropical Tropical Convergence Zone 129 (ITCZ) is neither zonally oriented, nor spatially fixed over the course of a year, thus wind fields are 130 highly variable in both strength and direction (Kessler, 2006). Further wind variability is introduced by low altitude jets blowing through three low elevation gaps in the Central American 131 132 Cordillera, with these jets observed predominantly between November and February (Kessler 2002, Fig. 1-schematically represented by orange arrows). These strong jet winds are generated from the 133 134 pressure gradient force resulting from high-pressure synoptic midlatitude weather systems transiting North America towards the low pressure Equatorial Pacific during the winter months (Chelton et al., 135 2001). Jet wind velocities of up to 20-30 ms<sup>-1</sup> have been observed within the three gulfs, extending 136 from the shoreline to at least 500 km into the ETPO (Chelton et al., 2001). The alignment of these 137 138 jets is mainly meridional in the Gulf of Panama and Tehuantepec, and more zonal in the Gulf of 139 Papagayo (Fig. 1). These jet winds result in strong wintertime upwelling in each of the three basins, 140 with the northerly jet winds in the Gulfs of Tehuantepec and Panama promoting Ekman upwelling (Kessler, 2006). At 9 °N, 90 °W, the quasi permanent anticyclonic Costa Rica thermocline dome is 141 142 energised by the westerly jet winds in the Gulf of Papagayo, again, resulting in upwelling (Fig 1. Kessler, 2002). However, the pressure disequilibrium that spawns these jet winds builds and 143 144 subsides quickly (on a sub-weekly timescale), resulting in a highly fluctuating jet wind field, and 145 nonlinearities in the oceanic (and hence upwelling) response to these episodic events (Kessler, 2006). Recent studies have shown that satellite SSS are very well suited to capture the variability of 146 147 these high SSS events (Grodsky et al., 2014; Reul et al., 2013).

During summertime, these jet winds are rare, and the northward deflection of the ITCZ over the ETPO result in very high levels of precipitation, particularly within the Gulf of Panama (Fig. 1; Alory et al., 2012). The effect of this rainfall is a strong freshening and stratification of the surface, especially in the Gulf of Panama region. For this reason, the Gulf of Panama is often referred to as the 'Pacific freshpool', with salinities of <30 frequently observed (Alory et al., 2012).

#### 2. Data and Methods

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# 2.1 Observations of in-situ fCO2 , DIC and atmospheric CO2

157 CO<sub>2</sub> data within the SOCAT database are recorded as fugacity of CO<sub>2</sub> (fCO<sub>2</sub>); a measure of pCO<sub>2</sub> 158 that is corrected for the non-ideal-gas behaviour carbon dioxide displays (Bakker et al., 2014). In 159 this study we will use fugacity of  $CO_2$ , owing to the improved accuracy of this measure over p $CO_2$ . The logistical importance of the region has proven beneficial, producing a large database of fCO<sub>2</sub>/ 160 161 SSS/SST observations, with  $\sim$  70,000 surface carbon, temperature and salinity data-points collected between 1991 and 2011 (within the region depicted in Fig. 1). We use data (converted from pCO<sub>2</sub> to 162 163 fCO<sub>2</sub>) collected between 1991 and 2013 within the LDEO v2013 database as a semi-independent dataset to test our SOCAT based statistical description of fCO2 within TS space (Takahashi et al. 164 165 2014). The LDEO database extends two years longer than SOCAT, making it a useful evaluation

We use SOCAT data as the basis of a statistical description of pCO<sub>2</sub> within the ETPO. All

166 product.

In addition to surface  $fCO_2$ , we use dissolved inorganic carbon (DIC) concentrations within the ETPO measured during World Ocean Circulation Experiment cruise P19 in 1993 (Fig. 1, WOCE data available from http://cchdo.ucsd.edu/), and weekly dry-air CO<sub>2</sub> mole fractions (xCO<sub>2</sub>) measured at Fanning Island ( $3.5^{\circ}$  N,  $159^{\circ}$  W, as part of the Scripps CO2 program,

171 http://scrippsco2.ucsd.edu/). We derive fCO<sub>2</sub> in the atmosphere according to:

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 $fCO_{2 air} = xCO_2 (p_{atm} - p_{H2O})$ (1)

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175 Where P<sub>atm</sub> is the atmospheric pressure taken from the ERA interim product

176 (www.apps.ecmwf.int/datasets/) and p<sub>H2O</sub>, the saturated water pressure (Weiss, 1974).

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## 178 **2.2. Calculating air sea fluxes of CO2**

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180 The air-sea flux of  $CO_2$  (mmol m<sup>-2</sup> d<sup>-1</sup>) is derived using the difference between surface 181 ocean and atmospheric fCO<sub>2</sub> values, the solubility of CO<sub>2</sub> in standard seawater ( $\alpha$  CO<sub>2</sub> calculated 182 using the values given by Weiss 1974) and the gas transfer velocity kCO<sub>2</sub> (cm/h):

183  $F = kCO_2 \alpha CO_2 (fCO_2 \text{ sea} - fCO_2 \text{ air})$  (2)

184 k is calculated using the 10 metre wind speed based parameterisation described by Sweeney et al.185 2007, where:

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$$k=0.27U^2(660/Sc)^{0.5}$$
 (3)

187 where Sc is the Schmidt number for  $CO_2$  (Wanninkhof, 1992). We use the 0.25°, daily resolution 188 10 m wind speed product from the Advanced Scatterometer (ASCAT,

189 <u>www.knmi.nl/scatterometer/</u>), and air  $fCO_2$  is calculated assuming water vapour saturation at the 190 boundary layer, then using the description in Eq. 1.

191 We note that when calculating air-sea gas exchange, it is not practical to derive a unique k parameter for all oceanic conditions and locations of interest, therefore, through necessity, k is 192 calculated using the non-specific parametrisation of Sweeney et al. 2007. Influences on k, such as 193 194 rainfall, have been observed to enhance gas transfer velocities in laboratory experiments (Liss and 195 Johnson, 2014). However, applying the results from these laboratory experiments into a modified 196 gas transfer velocity within the ETPO region is challenging, and requires further field experiments 197 to validate. It is for this reason, and the role rainfall has in reducing DIC, (thus bringing  $\Delta fCO2$ 198 closer to atmospheric equilibrium and limiting the influence on air sea fluxes brought about by an enhanced gas transfer velocity), we do not attempt to correct for the influence rainfall has on air-199 200 sea exchanges.

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### 202 2.3 Satellite observations of SST and SSS

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Sea surface temperatures have been continuously measured from space via satellites since the AVHRR mission in 1981, and sea surface salinity has been measured since the launch of the European Space Agency's Soil Moisture and Ocean Salinity (SMOS) satellite mission in November 2009 (Kerr et al. 2010). In this paper, we use satellite T and S data to help in the interpretation of spatial variability of  $fCO_2$  from the ETPO.

SMOS SSS maps at 0.25° resolution (running average over 100x100km<sup>2</sup>) produced by the LOCEAN SMOS group (combining SMOS ascending and descending passes) were used within this paper (Boutin et al. 2013, data available at www.cats.ifremer.fr/Products/Availible-productsfromCEC\_OS/Locean-v2013). SMOS SSS data are not used prior to June 2010 due to variations in sensor configuration tested during the in-orbit sensor commissioning phase (Corbella et al., 2011). Analysing the accuracy of the SMOS product, using in-situ point observations of SSS can be completed using both SOCAT SSS data (where the salinity is derived from ship mounted 216 thermosalinograph-TSG), and Argo profiles made within the region (S Fig. 1). Binning all Argo 217 and TSG near surface salinity data (that overlaps the SMOS observational period) into the same monthly, 0.25 degree structure as the SMOS monthly 0.25 ° product enables direct comparison. It is 218 219 found that the RMSE between SMOS and these binned in-situ data is 0.24 psu, with a minimal 220 offset (of 0.04 psu, S Fig. 1). This variability is a function of both the intrinsic variability of SSS within the EPTO (for example, caused by localised rainfall, riverine outflow, upwelling events that 221 222 may occur within each SMOS observational pixel), and a measurement error made in the SMOS 223 data. Estimates of this intrinsic variability within the tropics is 0.1 psu, but in certain regions (such 224 as the western warmpool and ETPO) may feature variabilities of 0.4 psu or higher (Delcroix et al. 225 2005). If the average intrinsic variability for the Tropical Pacific (of 0.1 psu) is used, the 226 measurement noise within the SMOS product is 0.14 psu. This measurement noise is included in 227 our fCO2 error estimates (as detailed below). We suggest that this is a satisfactory noise to signal 228 ratio, given that the region features SSS variability of upto 8 psu (Fig. 2). 229 SSS was combined with sea surface temperatures from the operational sea surface 230 temperature and sea ice analysis (OSTIA) system; an optimal interpolation of multiple microwave 231 and infrared satellite-based data sources (Donlon et al., 2012). This SST daily product features a

native resolution of 0.05°, which was subsequently re-sampled over the same spatial and temporal
grid as the SMOS data. As auxiliary datasets for near surface T and S, data from the Argo float
array were used.

#### 235 2.4 The basis of using a SST/SSS statistical fCO<sub>2</sub> model in the ETPO

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Using an fCO<sub>2</sub> model based on surface T and S properties requires the carbon properties of water masses to be quantified. We define three surface water-masses within the study region, based on the near-surface (0-100 m depth) T and S characteristics of the ETPO recorded by ~6000 Argo profiles between 17 °N and 4 °N, and east of 95 °W (Fig. 2). These water-masses are also independently featured within studies by Kessler (2002, 2006):

- 242 1)An ETPO surface water, with temperatures  $>27^{\circ}$ C and salinities >33.5 (Fig 2. 'B').
- 243 2)Deep water that predominantly exists below the thermocline (defined by Kessler as the 20
  244 °C isotherm) and is only expressed at the surface of the ETPO during periods of upwelling
  245 (Fig 2. 'C').
- 3)Rain influenced water, with salinities <33.5 (Fig 2. 'A').

247 Here, the water-mass at 'C' (referred to as 'deep water' herein) is predominantly found at 248 depths greater than 80 m, whilst the near surface water is typically ETPO surface water and warmer 249 than 27.5 °C ('A' and 'B'). Occasionally, the deep water-mass can be observed at shallower depths, 250 advected upwards during times of strong upwelling (Fig. 2). Rainfall influenced waters display a wide range of salinities (from 29 to 34.5) within the upper 20 m (as observed in the salinity 251 variation between 'A' and 'B'). At low salinities, densities as low as 1018 kg m<sup>-3</sup> are observed; an 252 eight kg m<sup>-3</sup> difference between this surface water and deep water (featuring densities of 1026 kg 253  $m^{3}$ ). This large density gradient is an important feature of the ETPO, as periods when stratification 254 255 and high thermoclines strengths are prevalent, the upwelling of deep water is inhibited (Fiedler and Talley, 2006). 256

257 To identify the carbon properties of these water-masses, DIC concentrations between the surface and 100 m depth within the ETPO measured during WOCE transect P19 are shown as red 258 circles and associated concentrations plotted within TS space (Fig. 2). Deep water 'C' was 259 observed to have DIC concentrations  $> 2200 \mu mol kg^{-1}$ , contrasting values between 'A' and 'B' of 260 <1950 µmol kg<sup>-1</sup>. End-member mixing occurs at intermediate temperatures between the two 261 262 watermasses 'B' and 'C', exhibiting in the gradient observed along the 34.2- 34.75 isohalines in 263 figure 2. Assuming that upwelling results in the expression of deep water at the surface, upwelling will act to increase the surface inventory of DIC, leading to increased fCO<sub>2</sub>. 264

Rainfall results in surface layer dilution, thus reducing DIC between 'A' and 'B' (Turk et al., 265 266 2010). When the  $fCO_2$  of both endmembers in this system (rainwater and surface waters) are at equilibrium with the atmosphere, this dilution results in a lowering of fCO<sub>2</sub> within the sea surface, 267 268 and ingassing of CO<sub>2</sub>. Turk et al's (2010) study in the western Pacific warm pool have indicated that decreases of 30- 40 µatm in surface fCO<sub>2</sub> values can result from rainfall alone, with these 269 270 effects strongest under highly stratified conditions. This suggests that rainfall could be an important 271 influence on ETPO fCO<sub>2</sub>, particularly within the rainfall dominated Panama Basin region. Finally, 272 although biological processes influence DIC (and hence fCO<sub>2</sub>), observations of DIC within this region suggest that physical processes (such as upwelling or rainfall) are the first order control on 273 DIC. For this reason, coupled to the lack of net community production data within the region, we 274 275 have elected to concentrate our efforts on quantifying these physical processes.

#### 276 2.5 Processing SOCAT data

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278 Surface  $fCO_2$  responds to changing levels of atmospheric  $fCO_2$ , which is increasing at 279 approximately 20 µatm per decade, (Takahashi et al. 2009, Fig. 3). In order to calculate

contemporary air sea fluxes, the multi-year SOCAT data must first be temporally corrected for the 280 281 inter-annual trend of increasing atmospheric CO<sub>2</sub>. The mean annual increase in fCO<sub>2</sub> within the 282 central equatorial Pacific (5 °N and 5 °S) between 1979 and 1990 (excluding El Niño events) was 283 estimated at a rate of 1.1  $\mu$ atm +/- 0.3 per year (Takahashi et al., 2009). A second estimate, using data collected between 1990 and 2003 (within the region 10 °N to 5 °S) calculated an annual 284 increase of 2.0 µatm +/- 0.2 (Takahashi et al. 2009). Correcting 1991 data to contemporary July 285 2014 values would equate to a not-inconsiderable difference depending on which of these two 286 287 estimates was chosen. Therefore, in order to choose the optimum correction for the smaller subregion of the ETPO, all available SOCAT fCO<sub>2</sub> data 1991-2011 were binned by year the data 288 289 was collected (Fig. 3). Fitting a linear regression to the average bin value of this data, resulted in an 290 average annual increase of 1.95  $\mu$ atm/ yr (+/- 0.38  $\mu$ atm). This linear regression was found to fall within the 5<sup>th</sup> and 95<sup>th</sup> percentile values for all bins, with variability in mean and median values 291 caused by heterogeneous sampling of the region and inter-annual variability (Fig. 3, percentiles 292 293 plotted in blue). Our calculated rate of increase is both within the range of the annual atmospheric fCO<sub>2</sub> increase measured at Fanning Island (1.8 µatm/ yr +/- 0.1 µatm) suggesting that fCO<sub>2</sub> within 294 the ETPO tracks the rate of increasing atmospheric  $fCO_2$  (Fig. 3). Therefore, we apply a 295 1.95 µatm per year correction to the SOCAT data in order to normalise the fCO<sub>2</sub> data to 1<sup>st</sup> July 296 297 2014 values, with all results herein also normalised to this date.

298 Although the spatial distribution of fCO<sub>2</sub> SOCAT observations within the ETPO are irregular, 299 the variability can be constrained once the TS properties of the surface ocean are accounted for (as-300 per DIC, Fig. 2, Fig. 4). Data from the upper 100 m of Argo profiles completed in each of the three 301 gulfs (Panama, Papagayo and Tehuantepec, as defined in Fig. 1) show strong TS similarities between each of the three gulf regions; low salinity (<34) waters are observed in each gulf, with a 302 303 thermocline separating surface-water and deep water at 80-100 m depth. The T-S properties of these Argo profiles are replicated at the surface, within SOCAT SST and SSS data (Fig. 4). 304 305 However, the relative numbers of observations that fall into each water-mass definition is different. The warm ETPO surface water is dominant in all three regions for the majority of samples, but 306 307 cooler (<20 °C) deep water is occasionally expressed at the surface, with this signal strongest in the 308 Gulf of Tehuantepec, followed by the Gulf of Papagayo, and seldom observed in the Gulf of 309 Panama. This contrasts observations of low salinity water, which are very frequent within the Gulf 310 of Panama, but rare in the other two gulfs (Fig. 4). Although both SOCAT and Argo data suffer 311 from sparse sampling, we suggest that both datasets indicate that the relative dominance of each 312 water-mass within each of the three gulfs is different. There are very few SOCAT observations

- 313 within the Offshore (OS) region (Fig. 1), thus we do not show a TS diagram from this region,
- however Argo profiles from this region are included in Fig. 2, highlighting that the OS also shares
- the same watermasses as the three gulf regions.
- The distribution of DIC concentrations within TS space is mirrored by fCO<sub>2</sub> values; deep
- 317 water features higher fCO<sub>2</sub> values than ETPO surface water, and low salinity water feature the
- 318 lowest fCO<sub>2</sub> values. The intermediate values of fCO<sub>2</sub> observed between each of these watermasses
- 319 suggest end-member mixing of fCO<sub>2</sub> between waters-masses. Finally, there are no watermasses that
- 320 share TS characteristics, but feature very different DIC concentrations or fCO<sub>2</sub> values, meaning that
- 321 DIC/ fCO<sub>2</sub> values are unique within TS space in this region (Fig. 2 and 4). Therefore, as both DIC
- 322 and fCO<sub>2</sub> values behave pseudo-conservatively within TS space, it is possible to construct a
- 323 statistical description of fCO<sub>2</sub> using solely SSS and SST.

#### 324 **2.6 Fitting a statistical description- the look-up-table**

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The similarities of T,S and fCO<sub>2</sub> properties of the water-masses observed both by Argo and within 326 the SOCAT database across all three gulfs enable data from the entire ETPO to be considered as a 327 single system (Fig. 5A). As the variance between individual fCO<sub>2</sub> observations occupying the 328 329 same location within T S space is low (Fig 5B) we use a look-up-table (LUT) to describe fCO<sub>2</sub> as 330 a function of T and S. This LUT technique, although not previously used to estimate oceanic fCO<sub>2</sub> has proven useful for estimating net primary productivity using satellite observations (Zhao et al. 331 332 2006). The LUT in this study uses a mesh of equal sized bins within T-S space. Observations of fCO<sub>2</sub> within these discrete TS bins are collected, and an average fCO<sub>2</sub> within TS space calculated. 333 334 As each bin is fully independent of neighbouring bins, non-linear and/or skewed fCO<sub>2</sub> distributions within TS space can be accounted for, and hence an improved synthetic fCO2 product, with a lower 335 336 root-mean-squared-error (RMSE) attained compared to using an alternative linear statistical 337 description, such as a basic linear fit.

338 By combining all SOCAT data from the ETPO onto a single T-S diagram, a look-up-table 339 (LUT) can be produced in order to describe fCO<sub>2</sub> as a function of T and S (Fig. 5). The LUT was 340 constructed by completing a linear interpolation of binned 0.1 (salinity) x 0.1 °C SOCAT data from 341 the entire ETPO region. The number of observations per bin is depicted in the right-hand panel. 342 Here, the highest number of observations fall in a narrow region of TS space, between salinities of 343 32-34.5 and 25-30 °C (Fig. 5). We tested the quality of fit of the SOCAT based LUT, using LDEO v2013 data. Here fCO<sub>2</sub> values were computed using the LUT using T and S from the LDEO v2013 344 345 database, with this computed fCO<sub>2</sub> data compared to the measured (annual increase corrected)

fCO<sub>2</sub> values. The LUT could be applied to 96.2 % of all LDEO v2013 T-S measurements made
between 1990 and 2013, with the remaining TS measurements falling outside the TS boundaries of
the LUT.

349 The average root-mean squared error (RMSE) of the LUT was 16.8 µatm between the LUT 350 computed and measured fCO<sub>2</sub>. This RMSE was asymmetrically distributed; highest at temperatures 351 of 22-26 °C/ salinities of 34.4, and lowest at warmer temperatures/ lower salinities and also at 352 colder temperatures (Fig. 5). This suggests that fCO<sub>2</sub> variability is low in aged surface waters, and 353 high in recently upwelled and warming water. As there are a number of measurements within the 354 region of higher error (Fig. 5), we hypothesize that this larger uncertainty is not due to lack of 355 observations, but rather to mixing / heating processes that allow water with slightly different fCO<sub>2</sub> 356 values to occupy the same TS space. For example, the fCO<sub>2</sub> value of water at salinities of 34.5 and 357 25 °C could either result from the stoichiometric mixing of two waters at salinities of 34.5, and temperatures of 18 and 32 °C, or solely from warmed 34.5 /18 °C water. Upwelling, solar radiation, 358 359 horizontal advection, biological productivity and diapycnal mixing processes all influence this 360 system, and need to be accounted for in order to quantify completely the formation and fCO<sub>2</sub> 361 observed within this water, but are outside the scope of this study using the data available in this region. However, this LUT technique works efficiently in determining the first-order variability of 362 the system within the ETPO. In order to calculate an uncertainty on this LUT derived synthetic 363 364 fCO2 data, we complete mean squared error calculation, based on the variance of fCO2 data within each cell of the LUT, and the uncertainty on SMOS SSS (as described above.) We assume that the 365 SST and SSS measurements within SOCAT, and the OSTIA SST product are accurate. This error is 366 367 propagated through the air-sea flux estimates in order to calculate an error on the air sea flux values 368 (as reported in table 1).

#### 369 3 Results

#### 370 **3.1 Bi-monthly variability along ship tracks**

Bimonthly  $fCO_2$  variability can be seen in the (1991-2011 annual  $fCO_2$  increase corrected) SOCAT observations plotted in figure 6. Here, the top six panels display SOCAT observations of fCO<sub>2</sub>, and the lower six panels display  $fCO_2$  calculated from SOCAT SST and SSS observations using the LUT. As the majority of SOCAT data is collected using ships of opportunity, resolution within shipping lanes in the ETPO is excellent; (for example multiple observations are made in regions south and west of the Panama Canal, at 9.1 °N, 79.7 °W ), but very sparse outside of these shipping lanes. However, acknowledging these issues in data resolution, patterns in  $fCO_2$  can still 378 be detected. The lowest fCO<sub>2</sub> is typically observed within the Gulf of Panama and close to the 379 coast. Higher fCO<sub>2</sub> is observed in the Gulfs of Tehuantepec and Papagayo. Inter seasonal variability 380 is also observed, with the highest fCO<sub>2</sub> (>440 µatm) occurring between November to February, with 381 lower fCO<sub>2</sub> values (<400 µatm) occurring across the entire region during the summer months (May-August). The data also show a very high degree of variability at small spatial and temporal scales, 382 383 for example during November- December within the Gulf of Papagayo. It is this variability that needs to be resolved using the LUT, when coupled to satellite SST and SSS observations at native 384 385 resolution. Thus, it is important to confirm that the LUT is able to recreate this variability in fCO<sub>2</sub> 386 using the initial (SOCAT) T and S conditions. Here, we find that the LUT performs well, with most 387 of the measured fCO<sub>2</sub> variability also observed within the fCO<sub>2</sub> calculated using the LUT (Fig. 6).

### 388 3.2 fCO<sub>2</sub> and fluxes by region- the influence of wind and upwelling

389 Using the LUT, SMOS and OSTIA data, the small scale variability and features within the 390 ETPO can be resolved more thoroughly than possible through SOCAT data alone. Bimonthly averaged (between July 2010- June 2014) SSS, SST, fCO<sub>2</sub>, CO<sub>2</sub> flux and windspeed are plotted in 391 392 figure 7. Jet wind velocities over the Gulf of Tehuantepec are at their peak between October to 393 February, thus optimising Ekman upwelling. During these months the SSS of the Gulf increases, whilst the SST decreases (due to the influences of upwelling). Increased fCO<sub>2</sub> is observed across 394 most of the Gulf of Tehuantepec, with peak outgassing occurring as a narrow band, centred 395 396 underneath the axis of the jet wind. We suggest that this is due to the complimentary nature of ocean physics in this region- high windspeeds promote Ekman upwelling of high DIC deep water, whilst 397 398 increasing the k component within the air-sea flux parameterisation, thereby maximising  $CO_2$ 399 outgassing.

400

#### 401 4 Discussion

402 The Gulf of Papagayo shares many similarities with the Tehuantepec Gulf, however, jet winds 403 are more zonally aligned (reducing Ekman pumping strengths, (Alexander et al., 2012)), and occur 404 later into winter compared to Tehuantepec; being strongest between November-February. This 405 results in a lag between peak wintertime  $fCO_2$  values seen within the two gulfs (Fig. 7 and 8). The 406 Gulf of Papagayo also features elevated fCO<sub>2</sub> values during the summer months which are not 407 seen in either the Gulf of Tehuantepec or Panama. This is due to westerly winds maintaining the 408 vorticity of the Costa Rican dome structure, enabling the continued upwelling of deep water at the 409 core of this dome throughout the summer season (Grodsky et al. 2014, Kessler 2006, Fig. 7).

The seasonally averaged wind velocities in the Gulf of Panama superficially resemble the wind patterns in the two northern gulfs- jet winds are observed between January- February (Fig. 7). However, excluding a small area of ocean directly underneath the wind jet axis during winter, the region remains a small net sink of carbon throughout the year (Fig. 8). We suggest that this contrast between the Panama gulf and the rest of the ETPO is due to the high rainfall within this region, resulting in the dilution of DIC as described above.

416

#### 417 **4.1 fCO<sub>2</sub> and the influence of rainfall**

418 A significant proportion of atmospheric water exported from above the Atlantic basin into the Pacific basin is precipitated into the ETPO. This rainfall is intensified within the ETPO during the 419 420 summertime, due to a northwards shift of the ITCZ towards the Panama coast (Xie et al., 2005). As 421 a result, the Gulf of Panama receives net precipitation of 180-220 cm per year, with peak rainfall of 422 20 mm per day during July-August (Alory et al., 2012). This large freshwater flux, coupled with light southerly winds between March and June, and the southerly (thus downwelling promoting), 423 424 winds between July and December result in the semi-permanent stratification of the water-column 425 (Fig. 7, Alory et al., 2012). Oualitatively, this stratification can be observed in the SOCAT and Argo data in Fig. 4 by the scarcity of deep water observations in the Gulf of Panama compared to the 426 Gulfs of Tehuantepec and Papagayo. Additionally, the thermocline is observed at deeper depths in 427 the Argo profiles taken in the Gulf of Panama, compared to either the Gulf of Tehuantepec or 428 429 Papagayo (Fig. 4).

430 The influence of stratification/ rainfall on fCO<sub>2</sub> values are seen in figure 7. Here, the lowest 431 salinity and fCO<sub>2</sub> are observed during the summer months (during peak rainfall season, Alory et al. 2012). This low fCO<sub>2</sub>, stratified system persists until January, when intensification of the south 432 equatorial current results in the export of the low fCO<sub>2</sub>/fresh surface layer towards the south west 433 434 (as seen by the elongation of the freshpool during January- March SSS). This export of water, 435 coupled with the dry-season within the Panama Gulf appears to weaken the stratification, with the result that sporadic jet winds enable Ekman upwelling, thus increasing SSS (Alory et al., 2012, Fig. 436 437 7) and average fCO<sub>2</sub> values between January-April (Fig. 8).

#### 438 **4.2 Air-sea fluxes from July 2010- June 2014**

439 The ETPO between 2010- June 2014 had an annual average  $\Delta$  fCO<sub>2</sub> 39.4 µatm (+/- 10.7) 440 and a outgassing CO<sub>2</sub> flux of 1.51 mmol m<sup>-2</sup> d<sup>-1</sup> (+/-0.41, Fig. 8/ Table 1). The ETPO, (the boundaries of which defined as per Fig. 1), has an area of  $1.9 \times 10^{12} \text{m}^2$ , therefore, net outgassing from the ETPO equates to  $10 \times 10^{12}$  g (0.01 Pg) of carbon per year.

To examine both monthly and inter-annual variability in air-sea fluxes, the ETPO is split into 443 444 subregions; the Gulfs of Tehuantepec, Papagayo, Panama and the Offshore region (Fig. 1, 8 and 445 Table 1). Here, although variable, the consistent seasonal cycle between summer and winter 446 observed in the bimonthly data in figure 7 is present for each individual year. Peak outgassing 447 within the Gulfs of Tehuantepec, Papagayo and the South Equatorial Current occurs during winter 448 (November -February). This contrasts the Gulf of Panama, which is a net sink of atmospheric CO<sub>2</sub> 449 except during occasional upwelling events during January -February. However, ingassing within of 450 the Gulf of Panama is insufficient to offset outgassing from the rest of the ETPO and the region 451 remains a net source of CO<sub>2</sub> year round.

452 In addition to seasonal variability, interannual variability is observed within the ETPO. Across 453 the entire basin, the ETPO during the years 2010-2012 were on average cooler and saltier than 454 subsequent years (especially 2012-13). This resulted in higher annually averaged outgassing and 455 fCO<sub>2</sub> values (Fig. 8, Table 1). Concurrently, during 2010-2012, the Gulf of Panama featured a low 456 salinity mimima (of 28), and a small freshpool footprint (the boundary of which is defined by the 457 33 isohaline (Alory et al., 2012)). The extreme low salinity observed within the eastern region of Gulf of Panama during 2010 to 2012 resulted in lower fCO<sub>2</sub> and hence stronger ingassing than 458 459 2012-2014 values, highlighting the effect of rainwater dilution of DIC. However, this localised 460 ingassing was insufficient to offset the higher outgassing observed in the other regions of the ETPO 461 (Fig. 8, Table 1). Also noteworthy is that average wind velocities were similar during 2010 and 462 2012 compared to subsequent years, so the increased outgassing observed during these years 463 cannot be attributed to increased wind-mediated Ekman upwelling of deep water alone.

464 We note that 2010 to the end of 2011 featured La Niña conditions, and suggest that this could 465 be causal to the differences in CO<sub>2</sub> fluxes, higher salinities and higher fCO<sub>2</sub> observed during this time period. A study using NCEP (National Centers for Environmental Prediction) reanalysis data 466 467 within this region observed cooler waters and more frequent upwelling of sub-thermocline deep 468 water during La Niña events. A shallower thermocline depth exists during La Niña events, which 469 results from the uplift of the water-column by intensified coastal Kelvin waves. Mechanistically, 470 this shallow thermocline reduces the strength of upwelling required for the expression of deep 471 water at the surface, thus decreasing average SSTs observed during La Niña periods (Alexander et 472 al., 2012).

Furthermore, Alexander et al's (2012) study also suggests that although jet winds are the first order control on SST and thermocline depth during winter; it is changes in the thermocline depth

475 (rather than changes in jet winds) that result in observed El Nino Southern Oscillation (ENSO)

476 variability in SST within the ETPO. Variability in thermocline depth, and by association,

477 variability in the ease by which deep water can be advected towards the surface suggest that

478 (ENSO) could drive variability within the surface fCO<sub>2</sub> observations. However, with only four

479 years of data, and no El Niño phase for intercomparision we are unable to draw definitive

480 conclusions.

#### 481 **4.3 Previous work**

The results in figures 7 and 8 represent the first attempt to quantify fCO<sub>2</sub> within the ETPO region at 482 483 high resolution from observations. Previous work encompassing the ETPO include three basin wide 484 or global fCO<sub>2</sub>/ pCO<sub>2</sub> studies, by Takahashi et al., (2009), Ischii et al., (2014) and Landschützer et 485 al., (2014). These studies, as discussed in the introduction, are based on the extrapolation of  $pCO_2$ 486 directly, or the extrapolation of pCO<sub>2</sub> using a neural network technique, and feature spatial resolutions of 4° x 5°, 4 °x 5° and 1° x 1° respectively. Of these three studies, only Takahashi et al. 487 488 (2009) features a dataset of calculated  $\Delta pCO_2$  that includes the ETPO region, thus allowing direct comparison with our calculations. Collocating the  $\Delta pCO_2$  results from Takahashi et al. (2009) 489 490 within the ETPO regions defined in Fig. 1, the Gulfs of Techuantepec, Papagayo, Panama and the 491 Offshore region featured values of +28.9, +54.1, +17.1 and +19.5 µatm respectively (Table. 1). This 492 suggests that the Takahashi et al. (2009) study differentiates the low  $\Delta pCO_2$  Panama Gulf region 493 from the higher values observed in the Gulfs of Tehuantepec and Papagayo. The resolution used in 494 Takahashi's study is too coarse to identify any mesoscale features (such as upwelling), or 495 interannual variability within the region. However, we find average  $\Delta pCO_2$  from Takahashi et al. 496 (2009) of 29.1 µatm was within the error limits of this study (Table 1). 497 Applying the same windspeed product, and gas transfer parametrisation used in this study to the ETPO  $\Delta pCO_2$  values from Takahashi et al. (2009), we find that all regions are net outgassing, with 498 499 the Gulf of Papagayo dominant within the ETPO (table 1). The ingassing observed within the Gulf 500 of Panama for our study is not replicated in Takahashi et al. 2009. The improved resolutions 501 featured in Landschützer et al., (2014) resulted in some mesoscale features being observed, such as 502 the increased pCO<sub>2</sub> values within the Gulf of Papagayo. However, this work was not able to identify the low pCO<sub>2</sub> conditions within the Gulf of Panama, most likely due to the same 503 504 biogeochemical province description being applied to the entire ETPO. In addition to these studies, 505 our work distinguishes the importance of jet winds in increasing pCO<sub>2</sub>, and quantifies the strong 506 inter annual variability within the region.

#### 507 **5. Conclusions**

508 Estimating surface fCO<sub>2</sub> and air sea fluxes of CO<sub>2</sub> within the global oceans has advanced considerably over the past decade, assisted by the assembly of large standardised atlases of surface 509 observations (such as the SOCAT database). However, although these databases boast 510 measurements in the millions, a challenge remains in gauging seasonal or sub-mesoscale fCO<sub>2</sub> 511 variability in the oceans. Sampling through the use of commercial volunteering observation vessels 512 513 may introduce bias, with most data existing within the narrow confines of the major global 514 shipping lanes or for only a few months of the year. However, the quantification of fCO<sub>2</sub> within TS space, used in conjunction with observations of surface SST and SSS (made possible through the 515 recent availability of SSS from satellite) has proved highly useful in improving our understanding 516 517 of fCO<sub>2</sub> variability at much improved spatial and temporal resolutions. We have demonstrated a 518 technique using SOCAT data to identify the fCO<sub>2</sub> signatures of water-masses within the ETPO region, namely, the high fCO<sub>2</sub> deep water, the near equilibrium ETPO surface water, and the 519 520 undersaturated rainfall diluted surface waters. From this, we used a LUT technique, in order to produce a description of the fCO<sub>2</sub> content of an ETPO surface water using satellite SST and SSS. 521 522 The highest outgassing and surface fCO<sub>2</sub> were observed during the winter period 523 (November -March), in the Gulfs of Tehuantepec, Papagayo and in the south equatorial current. 524 The first order control on these upwelling events and hence fCO<sub>2</sub> in the ETPO are strong wind jets blowing through low altitude gaps in the Central American cordillera. The Gulf of Panama 525 526 remained net undersaturated on average, due to dilution effects of heavy rainfall and the stratification of the water column. Although wind jets were observed in the Gulf of Panama, the 527 528 exceptionally low density of the water within this region appears to limit upwelling, and any 529 upwelling that occurs is directly underneath the wind jet axis. Inter-annual variability was observed 530 within the region, with the location of the western extent of the freshpool moving westwards

531 considerably between 2010 and 2014. Previous work within this region suggest that changes in

532 thermocline depth related to ENSO are likely to influence fCO<sub>2</sub> within this region. The region is a

533 net contributor to atmospheric  $CO_2$ , with average sea to air fluxes (over the four years of

observations) of 1.5 mmol  $m^{-2} d^{-1}$ , with all regions of the ETPO outgassing year-round, except

535 the rainfall diluted Gulf of Panama/ Freshpool region.

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- 638

639 Figure



## 640

641 Figure 1.

642 The topography of the Eastern Tropical Pacific Ocean and Isthmus of Panama, plotted using

643 GEBCO bathymetry. The three gulfs with the region, Panama (84° W to coastline of panama),

Papagayo (84 to 91 °W, north of 8 °N) and Tehuantepec (west of 91 °W, north of 10 °N), and the

645 Offshore region are marked in white. The transect of WOCE cruise P19 is indicated in purple. The

646 path of jet winds are marked by orange arrows.







649 The total library of Argo profiles collected within the ETPO in the upper 100 metres. Numbered red

650 dots indicate the total dissolved carbon concentration at specific TS values as measured during 651 cruise WOCE cruise p19.





665 Figure 3.

666 Yearly binned  $pCO_2$  measurements from the SOCAT database. The interpolated average rate of 667 ETPO fCO<sub>2</sub> increase is shown as a red line, with the atmospheric fCO<sub>2</sub> data shown as a green line. 668 The blue boxes represent the 5<sup>th</sup> and 95<sup>th</sup> percentile pCO<sub>2</sub>, with the small red lines indicating yearly 669 averages, and the red crosses yearly median.





TS data from the three main gulfs within the ETPO both from Argo floats (coloured by depth-top

three plots) and from surface SOCAT T and S data, (coloured by fCO<sub>2</sub> -bottom three plots).



685

686 Figure 5.

687 A, the Look Up Table derived from the position of ETPO SOCAT  $fCO_2$  measurements within T S 688 space.

- 689 B the root mean squared error of the LUT  $-fCO_2$  observations, showing the variance between  $fCO_2$ 690 observed within the same TS space in the LUT.
- 691 C the number of LDEO measurements per 0.1° x 0.1° salinity/ temperature bins that went into
   692 generating the LUT

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694

695



<sup>697</sup> 

- 699 SOCAT fCO<sub>2</sub> bimonthly (Jan+Feb, Mar+Apr, May+Jun, Jul+Aug, Sep+Oct, Nov+Dec)
- 700 observations within the ETPO corrected for the annual CO2 increas, LUT derived bimonthly fCO<sub>2</sub>
- 701 calculated using SOCAT SST and SSS observations and LUT-SOCAT observations

<sup>698</sup> Figure 6.





<sup>703</sup> Figure 7.

704	July 2010-	June 2014	average	SSS, SST,	LUT der	rived fCO <sub>2</sub>	, air sea	fluxes	and wind	vectors for

705 the ETPO, split bimonthly (Jan+Feb, Mar+Apr, May+Jun, Jul+Aug, Sep+Oct, Nov+Dec).



<sup>706</sup> 

- 708Upper: Yearly average SSS, SST LUT derived  $\Delta fCO_2$ , air sea fluxes and wind vectors for the ETPO709for July to June 2010+2011, 2011+2012, 2012+2013 and 2013+2014.
- 710 Lower: The continuous LUT derived fCO<sub>2</sub> fluxes from the entire ETPO (red line), the Gulfs of
- 711 Tehuantepec (purple), Papagayo (blue), Panama (green) and the South Equatorial Current (black).
- 712
- 713

<sup>707</sup> Figure 8.



722 Supplementary Figure 1.

Monthly 0.25 degree SMOS SSS matchups with near surface Argo and SOCAT TSG data (that have
been binned into the same monthly/ 0.25 degree grid as the SMOS SSS data). The red error bars
indicate the standard deviation, the blue line is a linear regression between the two SSS datasets.

Table 1.

Annual averaged values for each region, as reported in figure 8 and average values from Takahashi et al. 2009. 

			CO2 Flux			
		CO2 Flux	error (+/-			
	Δ fCO2	(mmol m-2	mmol m-2 d-	Wind		Temp
Date/ Location	(µatm)	d-1)	1)	(ms-2)	Salinity	(°C)
2010-11 ETPO	40.4	1.55	0.39	4.81	33.3	27.9
2010-11 OS	41.1	1.62	0.40	5.18	33.2	27.7
2010-11 Panama	-4.7	-0.19	-0.03	4.57	28.3	27.4
2010-11 Papagayo	34.8	0.95	0.20	4.17	33.7	28.2
2010-11 Tehuantepec	40	1.55	0.33	3.72	33.6	29.0
2011-12 ETPO	42	1.56	0.43	4.59	33.3	27.9
2011-12 OS	43.2	1.60	0.48	4.97	33.1	27.7
2011-12 Panama	-4.1	-0.21	0.05	4.02	28.4	27.5
2011-12 Papagayo	34.1	1.09	0.34	4.01	33.7	27.9
2011-12 Tehuantepec	49.3	1.64	0.36	3.90	33.7	28.4
2012-13 ETPO	35.3	1.41	0.40	4.88	33.2	28.6
2012-13 OS	37.1	1.50	0.43	5.11	33.0	28.3
2012-13 Panama	-2.1	-0.11	0.08	3.92	28.7	27.3
2012-13 Papagayo	32.8	1.08	0.37	4.49	33.6	28.5
2012-13 Tehuantepec	32.5	1.52	0.43	4.08	33.6	29.3
2013-14 ETPO	39.9	1.53	0.41	4.67	33.3	28.0
2013-14 OS	39.3	1.63	0.45	5.09	33.0	27.8
2013-14 Panama	-2.8	-0.16	0.05	3.88	27.5	27.7
2013-14 Papagayo	37.9	1.15	0.38	4.15	33.7	28.0
2013-14 Tehuantepec	47.7	1.57	0.43	3.92	33.7	28.6
Average ETPO	39.4	1.51	0.41	4.7	33.3	28.10
Average OS	40.2	1.59	0.44	5.1	33.1	27.88
Average Panama	-3.4	-0.17	0.04	4.1	28.2	27.48
Average Papagayo	34.9	1.07	0.32	4.2	33.7	28.15
Average Tehuantepec	42.4	1.57	0.42	3.91	33.7	28.83
Takahashi 2009. ETPO	29.1	0.78	N/A	4.74	33.3	28.10
Takahashi 2009. OS	19.5	0.65	N/A	5.09	33.1	27.88
Takahashi 2009. Pan	17.1	0.54	N/A	4.10	28.2	27.48
Takahashi 2009. Pap	54.1	1.83	N/A	4.21	33.7	28.15
Takahashi 2009. Tec	28.9	0.71	N/A	3.91	33.7	28.83