TPOS Whitepaper #6
Tropical Pacific Biogeochemistry: Status, Implementation and Gaps

Jeremy T. Mathis, Richard A. Feely, Adrienne Sutton, Craig Carlson, Fei Chai, Francisco Chavez, Matt Church, Catherine Cosca, Masao Ishii, Calvin Mordy, Akihiko Murata, Joe Resing, Pete Strutton, Taro Takahashi, and Rik Wanninkhof

1.0 Introduction

The oceans play an important role in the climate system as a large sink for anthropogenic carbon dioxide (CO_2), and, thereby partially mitigate the large-scale effects of humankind's CO_2 emissions into the atmosphere. As a whole, the oceans take up approximately 2.6±0.5 Pg C year^{-1} of the 8.6±0.4 Pg C year^{-1} that are emitted from the burning of fossil fuels. As such, the oceans absorb about 24 million tons of CO_2 every day or roughly 4 kg per day for every person on Earth.

Estimates of the net sea-air CO_2 flux based on measurements of partial pressure of CO_2 (pCO_2) in near-surface seawater and in the marine boundary air show that the extra tropics are major oceanic sinks of atmospheric CO_2 and the tropics are major sources. The tropical ocean is the ocean's largest natural source of CO_2 to the atmosphere and the annual contribution of CO_2 to the atmosphere from the oceanic equatorial belt is estimated to be between 0.6–1.0 Pg C (Takahashi et al., 1999, 2002, 2009; Wanninkhof et al., 2013). Despite comprising a net source of CO_2 to the atmosphere, equatorial waters are characterized by relatively high rates of primary productivity and serve as globally significant regions of biologically-fueled carbon sequestration to the deep sea. However, changes in ocean circulation patterns along with regional and global-scale climate processes may significantly impact the biogeochemistry of equatorial regions and alter the uptake rates of CO_2 on decadal or longer time-scales. Given the role that this region plays in determining atmospheric CO_2 concentrations, it is critical to determine;

1. Will the ocean carbon sinks keep pace with increasing anthropogenic CO_2 emissions?
2. How does oscillation between El Niño/La Niña events impact the delivery of nutrients to the mixed layer and the production, transport and fate of biogenic carbon?

Here, we provide the justification for answering these questions and lay the groundwork for how to carry out the necessary observations as part of the Tropical Pacific Observing System (TPOS) 2020 effort.

2.0 Background

2.1 The Role of the Tropical Ocean in the Global Carbon Cycle

The mean circulation of the equatorial Pacific Ocean is characterized by upwelling that brings cold nutrient- and carbon-rich water to the surface along the equator east of about 160°W during non-El Niño periods. The primary source of the upwelled water along the equator is the narrow Equatorial Undercurrent (EUC), which flows eastward across the basin. This mean circulation and its seasonal variations are

significantly modulated on interannual and decadal time scales by two prominent modes of natural variability: (1) the El Niño-Southern Oscillation (ENSO) cycle; and (2) the Pacific Decadal Oscillation (PDO). The warm El Niño phase of the ENSO cycle is characterized by a large-scale weakening of the trade winds, decrease in upwelling of carbon dioxide (CO_2) and nutrient-rich subsurface waters and a corresponding warming of the sea surface temperature (SST) in the eastern and central equatorial Pacific (McPhaden et al., 1998). Carbon-14 (C-14) data suggest that the high-CO_2 water of the EUC originates in the pole-ward edge zone of the subtropical gyres (possibly both in the northern and southern hemispheres). The bomb C-14 concentration in the atmosphere peaked around 1965. This was detected in the 100-meter deep western equatorial Pacific water about 8 years later and propagated eastward via the undercurrent reaching the Galapagos area about 13 years after the atmospheric peak (Mahadevan, 2001). This suggests that the pCO_2 in the upwelling waters during La Niña events includes the atmospheric CO_2, which was absorbed by high-latitude low-pCO_2 waters in the past decade, as well as the CO_2 respired from biogenic debris released back into the atmosphere during the La Niña events. Thus, CO_2 in the upwelling water in the equatorial Pacific is a complex mixture of CO_2, which may vary with time reflecting physical and biological responses to climate change.

El Niño events occur roughly once every 2–7 years and typically last about 12–18 months. The opposite phase of the ENSO cycle, called La Niña, is characterized by strong trade winds, cold tropical SSTs, and enhanced upwelling of CO_2-rich water along the equator (Figure 1). El Niño and La Niña are associated with dramatic shifts in the atmospheric pressure difference between the eastern and western Pacific (referred to as the Southern Oscillation) that have major impacts on the climate variability worldwide (McPhaden, 1999) and on the sources and sinks for CO_2 in the atmosphere and oceans. The PDO has been characterized either in terms of fluctuations over a broad band of periods between 10–70 years (Minobe, 2000), or in terms of abrupt temporal "regime" shifts in climate conditions and ecosystems over large parts of the basin (Mantua et al., 1997) with the most recent of these regime shifts occurring in 1976–1977, 1988–1989, and 1998 (Trenberth et al., 1996; Watanabe and Nitta, 1999; Beamish et al., 1999; Hare and Mantua, 2000; McPhaden and Zhang, 2002; Chavez et al., 2003; Takahashi et al., 2003; McPhaden and Zhang; 2004).

For example, both Hare and Mantua (2000) and Wang et al., (2006) found evidence for the 1989 regime shift from time-series of a number of physical, biological and chemical parameters in the North Pacific. In the tropics, the 1976–1977 regime shift was characterized by a slowdown of the shallow meridional overturning circulation and a warming of the sea surface by nearly 1°C in the cold tongue region of the eastern and central equatorial Pacific Ocean (McPhaden and Zhang, 2002). The most recent shift, which occurred in the 1997–1998 period, was characterized by an enhancement of the meridional transport and a slight decrease in SST (McPhaden and Zhang, 2004). On the other hand, based on a coupled atmosphere-ocean model, Rodgers et al., (2004) suggested that nonlinearities in ENSO variability can play an important role in determining the structure of tropical Pacific variability on decadal time scales. Thus, it is still open to debate whether the decadal modulation of ENSO is a cause of, or effect of,

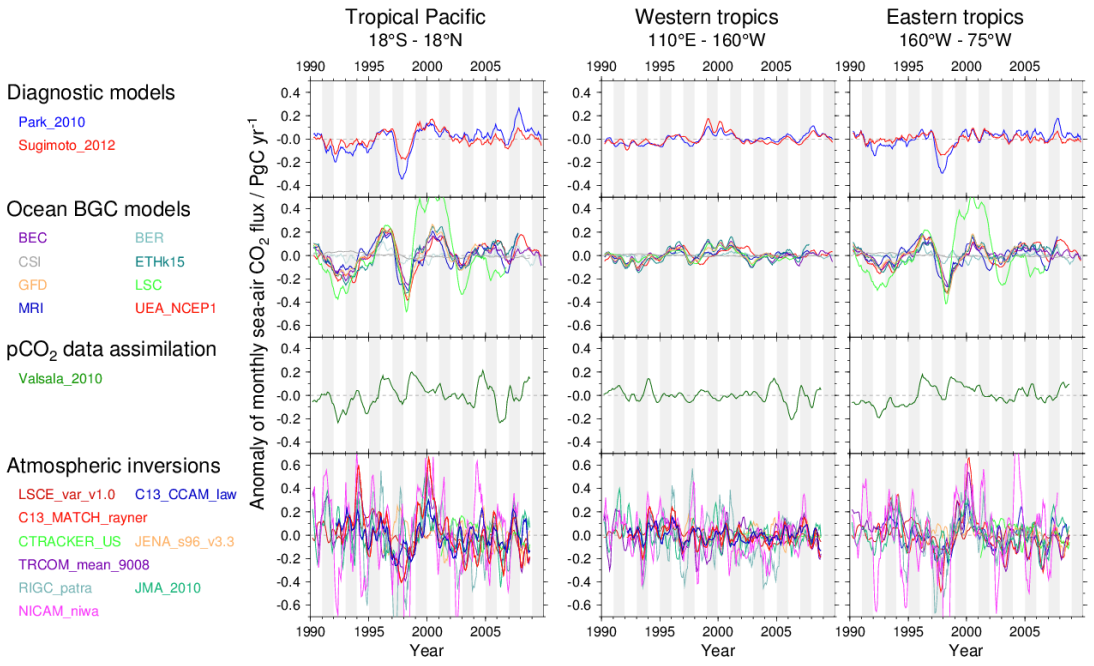

Figure 1. Trends of sea-air CO_2 flux anomalies (5-month running mean, positive is flux out of the ocean) in the tropical Pacific (18°S – 18°N) for 1990 – 2009 (after Ishii et al., 2014).

the PDO.

Table 1 – Sea-Air CO_2 Flux (Pg C yr^{-1}) by Basin.

Latitude Band	Pacific	Atlantic	Indian	Southern	Global

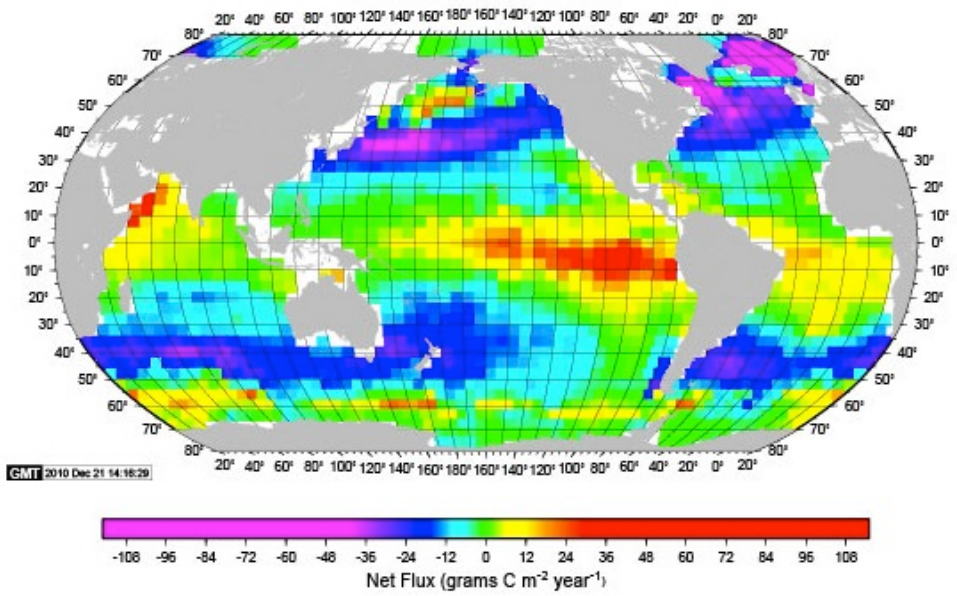

Figure 2. Climatological mean sea-air CO_2 flux (g C m^{-2} yr^{-1}) for the reference year 2000 (non-El Nino conditions; updated after Takahashi et al., 2009).

Table 1. Net sea-air CO_2 flux (in Pg C yr^{-1}) by ocean basin and latitude band,

N of 50°N	-0.03	-0.26			-0.29
14°N-50°N	-0.50	-0.22	+0.02		-0.69
14°S-14°N	+0.48	+0.10	+0.10		+0.68
14°S-50°S	-0.41	-0.20	-0.41		-1.02
50°S-62°S				-0.05	-0.05
Total	-0.46	-0.58	-0.29	-0.05	-1.37
% of Uptake	34	42	21	3	100

2.2 Interannual and Decadal Variability of Sea-air CO_2 Fluxes

As a direct consequence of the extensive amount of physical, chemical and biological research of the tropical oceans over the past 30-40 years, it is well known that this region, particularly the central and eastern equatorial Pacific, exhibits a large amount of spatial and temporal variability in ocean biogeochemical processes and properties. Much of this variability appears attributable to tightly coupled ocean-climate interactions in this region. Interannual to decadal scale variations in trade wind forcing control the strength of upwelling in this region, resulting in modification to air-sea CO_2 fluxes (Figure 2), nutrient supply, and ultimately biological productivity in the region. As a result, pCO_2 and sea-to-air CO_2 fluxes demonstrate large variability over interannual to decadal time scales (Feely et al., 1999, 2002, 2006; Ishii et al., 2004, 2011, 2014; Takahashi et al., 2003, 2009; Wanninkhof et al., 2013; Sutton et al., 2014).

Studies based on the long time-series measurements of chemical and biological measurements collected from ships and moorings associated with the Pacific Tropical Atmosphere Ocean (TAO) mooring array have delineated that the central and eastern equatorial Pacific are major sources of CO_2 to the atmosphere (Table 1) during non-El Niño and La Niña periods; it is near neutral during strong El Niño periods, and a weak source during weak El Niño periods. On decadal time scales, the Pacific Ocean has undergone major physical and biological regime shifts commonly referred to as the Pacific Decadal Oscillation (PDO), which has been documented on the basis of extensive physical and biological data (Trenberth et al., 1996; Hare and Mantua, 2000; McPhaden and Zhang, 2002; Chavez et al., 2003; McPhaden and Zhang; 2004; Chavez et al., 2011). While the causes and effects of these regime shifts have been investigated in recent years, only a few long-term studies of its effect on primary productivity, CO_2 chemistry, and nutrient supply in the equatorial Pacific have been conducted (Takahashi et al., 2003; Feely et al., 2006; Chavez et al., 2011; Ishii et al., 2014). Such studies demonstrate the sensitivity of these regions to climate variability, including documenting long-term (decadal-scale) changes in primary production and the growth rate of CO_2 in surface waters and an overall decline in pH, referred to as ocean acidification (Sutton et al., 2014).

While ENSO drives much of the interannual variability in the outgassing of CO_2 in the equatorial Pacific, the PDO, the strength of ENSO events, and the location of the SST anomalies during El Niño events also play important roles. During the strong El Niño events of 1982-1983 and 1997-1998, upwelling ceased at the Equator along with CO_2 outgassing as the pCO_2 in surface waters reduced to equilibrium with respect to the

atmosphere (Chavez et al., 1999; Feely et al., 1987, 1999, 2002, 2006). In fact, in early 1998, moored pCO_2 measurements from the central equatorial Pacific showed that the region became a weak sink of CO_2 (Chavez et al., 1999). Weaker El Niño events have dominated in the period since, and some suggest that a PDO regime shift after the 1997-1998 El Niño has caused increasing trade winds, shallower thermocline, rebound of the shallow meridional overturning circulation, and increasing frequency of La Niña events (Chavez et al., 2003; Feely et al., 2006; Ishii et al., 2009, 2014; McPhaden, 2012; McPhaden and Zhang, 2004; Peterson and Schwing, 2003; Takahashi et al., 2003; Sutton et al., 2014; Feely et al., in preparation; Cosca et al., in preparation). In addition, El Niño events post 1997-1998 have been central Pacific (CP) events (also referred to as "date line", "warm pool", or "El Niño-Modoki" events), where the largest SST anomalies occur in the central Pacific instead of in the eastern Pacific during traditional El Niño events (Ashok et al., 2007; Kao and Yu, 2009; Kug et al., 2009; Larkin and Harrison, 2005). These events impact the distribution of sea surface conditions across the equatorial Pacific, influencing seawater pCO_2 and SST conditions and the outgassing flux of CO_2 to the atmosphere particularly during El Niño events. Since this regime shift, CO_2 outgassing by the ocean has increased ~25-30% (Feely et al., in preparation).

2.3 Primary Production and Nutrient Dynamics

The equatorial Pacific is a globally significant region of ocean production, with rates of net primary productivity estimated between 9 and 14 Pg C yr^{-1}. Moreover, export production, the fraction of organic matter production that escapes upper ocean remineralization and hence contributes to biological carbon sequestration, has been estimated ~0.7-2.5 Pg C yr^{-1} (Chavez and Barber 1987; Behrenfeld et al. 2006). Gravitational settling of particulate organic matter, physical redistribution (via mixing, advection and subduction) of dissolved organic carbon, and zooplankton vertical migration are the prominent mechanisms driving vertical fluxes of organic matter from the well-lit upper ocean across the thermocline. The upper ocean waters of the eastern and central regions of the equatorial Pacific have been broadly characterized as high nutrient-low chlorophyll (HNLC) habitats, where concentrations of inorganic macronutrients (specifically nitrate) are perennially elevated. The HNLC condition implies the physical supply of nutrients to the upper ocean (primarily via upwelling in equatorial waters) exceeds the rate of biological removal of these nutrients.

Various factors have been identified as controlling phytoplankton consumption of macronutrients in this region and hence limiting export production in the equatorial Pacific; these include trophodynamic processes (*i.e.* grazing control of phytoplankton biomass) and nutrient supply and availability, most notably including the supply of iron (Landry et al., 2011; Coale et al. 1996; Behrenfeld et al. 1996). Thus, understanding the sensitivity of biological carbon drawdown in this region to changes in ocean-climate will require detailed, time-resolving measurements of air-sea interactions, vertical and Aeolian nutrient supply, and primary production and phytoplankton biomass.

Primary productivity in the tropical Pacific is regulated both by macronutrients (e.g., nitrate) and by trace nutrients with iron (Fe) most often being the limiting nutrient in the open ocean. Fe is transported to most of the open ocean by atmospheric transport

of aerosols from the continents to the surface ocean. However, near the equator there is little transport of aerosol Fe and additional sources are required to sustain primary productivity. Transport of iron from the western to eastern Pacific by the EUC is one possible source (Ryan et al., 2006; Slemons et al., 2010). Models suggest that western Pacific sources of dissolved iron delivered via the EUC are important in sustaining annually integrated equatorial Pacific primary production; short term variations in this Fe source do not appear to constrain the timing of modeled central and eastern Pacific plankton blooms (Gorgues et al., 2010), but the ecological impact in the eastern Pacific from long- and short-term variability in equatorial undercurrent iron sources remains to be shown.

To date, a single study conducted over a 45 day interval has documented this transport; in that study the maxima in Fe in the eastern tropical Pacific was just below the core of the undercurrent (~200m). If this maximum is perpetually at this depth then the depth of the thermocline and strength of the equatorial upwelling that are important in the release of nutrients to the euphotic zone of the eastern Pacific are even more important for transporting the limiting trace nutrient Fe into the photic zone. Meanwhile, waters in the EUC are generally < 1 year old and reflect the variability of its source waters on both short and long time scales. How this variability is superimposed upon thermocline depth and strength of upwelling is largely unknown and remains an important question. However, the depth and magnitude of the source must play a role in the depth of Fe transport within the EUC and it has been suggested that this has directly affected primary productivity (Ryan et al., 2006). This variability depends in some ways on the seasonal and interannual variability of the major western boundary currents feeding the EUC (e.g., the New Guinea Coastal Undercurrent (Cresswell, 2000). Sources of Fe include sediment resuspension, riverine runoff, hydrothermal activity and anthropogenic sources like subaerial and eventually submarine mining. Ultimately, the modulation and variability of Fe input and mobilization within the pathways of these source currents and the subsequent transport of these iron-enriched waters might act as a throttle on productivity in the central and eastern equatorial Pacific and may also act to regulate carbon export from this region.

While new monitoring efforts have helped to reduce uncertainties in the sea-air flux of CO_2, large uncertainties remain in our understanding of the export flux of particulate organic carbon (POC) from the euphotic zone to the interior of the ocean – ranging from ~4-6 Pg C yr^{-1} (Gehlen et al., 2006; Henson et al., 2010; Moore et al., 2004; Lutz et al., 2007; Siegel et al., 2014) to ~10-12 Pg C yr^{-1} (Dunne et al., 2007; Gehlen et al., 2006; Laws et al., 2000) (Figure 3). Even higher values are necessary to balance rates of heterotrophic respiration in the deep ocean (e.g. Burd et al., 2010). These uncertainties are driven by differences in the methods used to determining the export ratio (e.g. f-ratio, ^{234}Th), the parameterization of sparse data sets that are globally extrapolated using satellite SST, and the influence of environmental and biological factors on sinking rates of POC (e.g. fraction of diatoms, packaging effects, biogenic minerals that may act as ballast; Armstrong et al., 2002; François et al., 2002) among other factors.

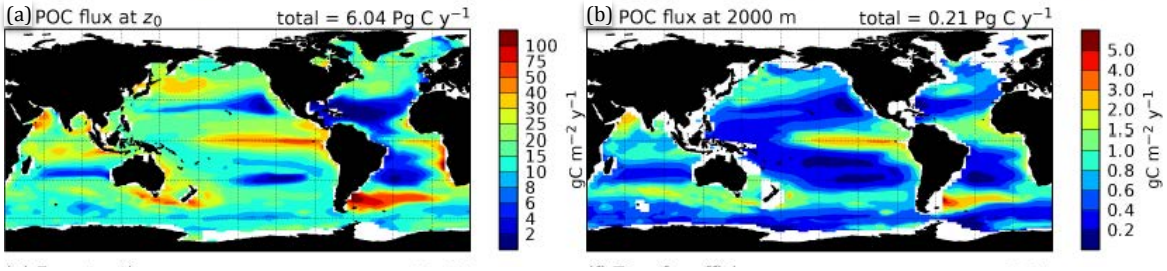

Figure 3. Modelled flux of POC at a) the export depth (Z_0) and b) 2000m (Lima et al. 2014). The export depth was computed as the depth where POC production is 1% of maximum POC production in the water column, and varied from 50-300 m in the global ocean.

Some of the highest rates of POC export are found in the eastern tropical Pacific (Figure 3; Siegel et al., 2014) where shoaling of the nutricline (Figure 4) supports very high rates of primary production (reviewed by Pennington et al., 2006). In this region, both Fe and $Si(OH)_4$ influence new and export production of diatoms – with Fe regulating production of organic matter, and $Si(OH)_4$ regulating silicification (i.e. frustual thickness) (Brzezinski et al., 2008).

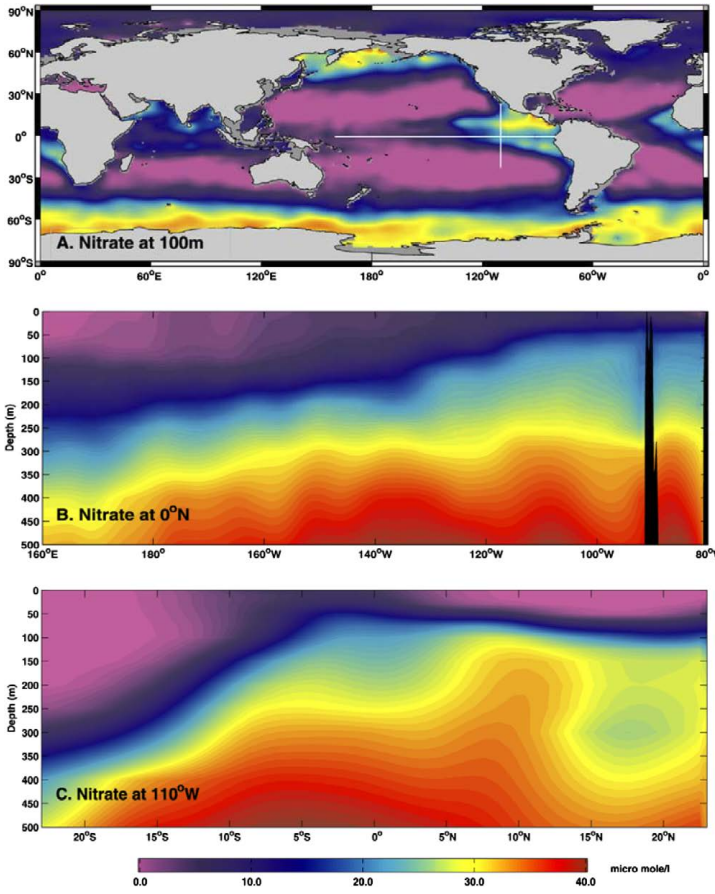

Figure 4. Distribution of nitrate in the Eastern Tropical Pacific as shown by Pennington et al., 2006. (A) Global 100 m nitrate. The white lines indicate the positions of panels B and C. 100 m nitrate is near zero in the subtropical gyres and at the western boundaries, but higher at the eastern boundaries, at high latitudes, and in the eastern tropical Pacific; (B) Vertical section of nitrate along the equator. The equatorial thermocline tilt causes near-surface nitrate to be higher in the east; (C) Vertical section of nitrate on 110°W showing basin-scale nutricline shoaling across the equator associated with the subtropical gyre circulation.

As the nutrient supply and export production is sustained by southeasterly trade winds,

the ENSO cycle plays a major role in controlling the export flux of biogenic carbon out of the euphotic zone. A synthesis of the Joint Global Ocean Flux Study (JGOFS) in the equatorial Pacific during 1992 revealed that the export flux of total organic carbon was four-times higher during the fall non-El Niño period as compared with the Spring El Niño event (Quay, 1997). Behrenfeld et al. (2006) observed strong correspondence between fluctuations in ENSO and satellite derived net primary production in this region, with subdecadal scale increases in net primary production during cold phase ENSO cycles, with reduced rates of productivity occurring during warm phases. Recent studies by Chavez et al. (2011) have also demonstrated that primary production is also affected by the changes in the physical dynamics of upwelling and thermocline mixing processes during the warm and cold phases of the ENSO cycle (Figure 5). Their results show that the biogenic carbon fluxes are directly responding to the phasing of the ENSO cycle by taking up more nutrients into phytoplankton during the cold phase of the ENSO cycle when upwelling is strong and nutrient inputs are highest. In the same manner, the primary production appears to be increasing over the past several years, consistent with the recent PDO shift to cooler conditions and more extensive upwelling (Chavez et al., 2011). In addition, dissolved organic carbon (DOC) is thought to contribute ~20% to carbon export in the global ocean (Hansell et al., 2009).

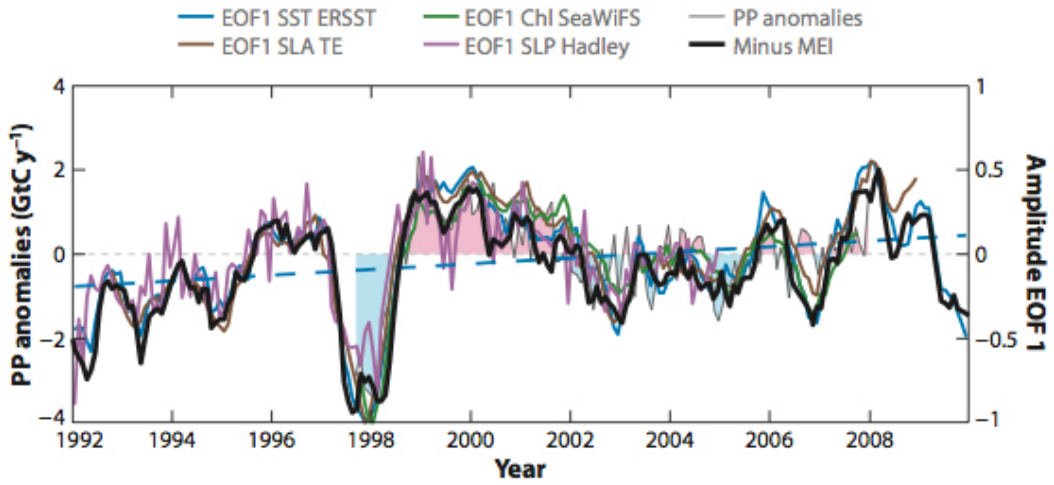

Figure 5. Global primary production anomaly (PPA) and first empirical orthogonal function (EOF) modes of seasurface temperature (SST), sea level anomaly (SLA), sea level pressure (SLP), chlorophyll (logChl), and the normalized Multivariate ENSO Index (MEI).

Dissolved organic matter (DOM) represents one of the largest exchangeable reservoirs of organic material on earth. At ~662 ±32 Pg (10^{15} g) C (Hansell et al., 2009, dissolved organic carbon (DOC) exceeds the inventory of organic particles in the oceans by 200 fold, making it one of the largest of the bioreactive pools of carbon in the ocean, second only to dissolved inorganic carbon. Photoautotrophic production fixes CO_2 to organic matter, which in turn serves as a substrate that fuels the oceanic food web. As that organic matter is produced and processed within the oceanic food web a portion is

released into the dissolved organic matter (DOM) pool. Most of the freshly produced DOM is consumed rapidly by heterotrophic microbes but some escapes remineralization or is further transformed into recalcitrant forms of DOM that accumulates and can persist in the oceanic water column for months (semi-labile DOM) to millennia (refractory DOM) (Carlson 2002, Hansell and Carlson 2012, Benner and Herndl 2011, Goldberg et al., 2011). The recalcitrant DOM pools are biogeochemically relevant because they can be physically transported via ocean currents and mixing, thus contributing significantly to vertical and horizontal export of organic carbon, nitrogen within the oceanic water column (Hansell et al. 2009; Letscher et al., 2013).

As described above, the Equatorial Pacific is a significant source of CO_2 to the atmosphere, but it also contributes considerably to the global ocean's new production. Estimates of new production within the equatorial Wyrtki box (5°N – 5°S) range between 0.61 Pg C y^{-1} (Wang et al. 2006) and 1.9 Pg C y^{-1} (Chavez and Barber 1987) or ~ 5- 20 % of global new production (~ 10 Pg C y^{-1}; Chavez and Toggwelier, 1995). New production is partitioned between particulate organic matter (POM) and DOM each of which has a vastly different effect on export of organic matter in this system. Using mass balance techniques Hansell et al. (1997) estimated that vertical POM flux dominated organic matter removal from the surface waters accounting for approximately 80% of net community production in equatorial Pacific with the balance accumulating as DOM in the surface waters. The DOM that escaped rapid microbial remineralization and accumulated in the surface water was available for horizontal advection from the equatorial Pacific into the subtropical gyres (Figure 6). Estimates of poleward advection of DOM from the Wyrtki box range from a low range of 0.7 – 0.18 Pg C y^{-1} (Hansell et al. 1997) up to 0.4 Pg C y^{-1} (Archer et al., 1997) as DOC and 0.03 Pg N y^{-1} as DON (Hansell et al., 1997). The build up of semi-labile DOC in the subtropical gyres (Figure 6) as a result of autotrophic production in the gyres as well as horizontal advection of DOM from the equatorial Pacific can be exported into the interior by Ekman convergence of surface waters and downwelling of DOC-rich waters to a few hundred meters depth.

Techniques have greatly improved over the past two decades with regard to DOM analyses and the US Repeat Hydrography program has allowed for the first ever high-resolution ocean DOM maps and inventory. Yet, there is still a paucity of DOM data especially in the equatorial Pacific. It would be beneficial to obtain measurements in this important region to better estimate the role of DOM in both horizontal and vertical export from this important oceanic region.

Sustained observations in the equatorial Pacific have been critical to improving our understanding of the ENSO cycle and its interaction with other modes of large-scale climate variability in this region and around the globe (McPhaden et al., 2006). While many global biogeochemical models, ocean carbon cycle models, and atmospheric inversions are able to capture the interannual variability of sea-air CO_2 fluxes in the equatorial Pacific (Rayner et al., 1999; Jones et al., 2001; Patra et al., 2005; Le Quéré et al., 2010), separating natural variability from global change impacts and understanding how these phenomena will interact in the future is challenging. Climate change predictions in the equatorial Pacific include warming sea surface temperatures,

weakening trade winds, and a shoaling thermocline; however, it is unclear whether the frequency or intensity of ENSO events may change (Vecchi et al., 2006; Collins et al., 2010). Some researchers link an increased frequency of CP El Niño events to anthropogenic climate change (Yeh et al., 2009), while others suggest the observed increase since 1997–1998 is part of a natural variation of the climate system (McPhaden et al., 2011; Newman et al., 2011). Continued investigation into the interannual, decadal, and multi-decadal dynamics that impact the equatorial Pacific is key to understanding how ENSO and CO_2 outgassing in this region may change in the future.

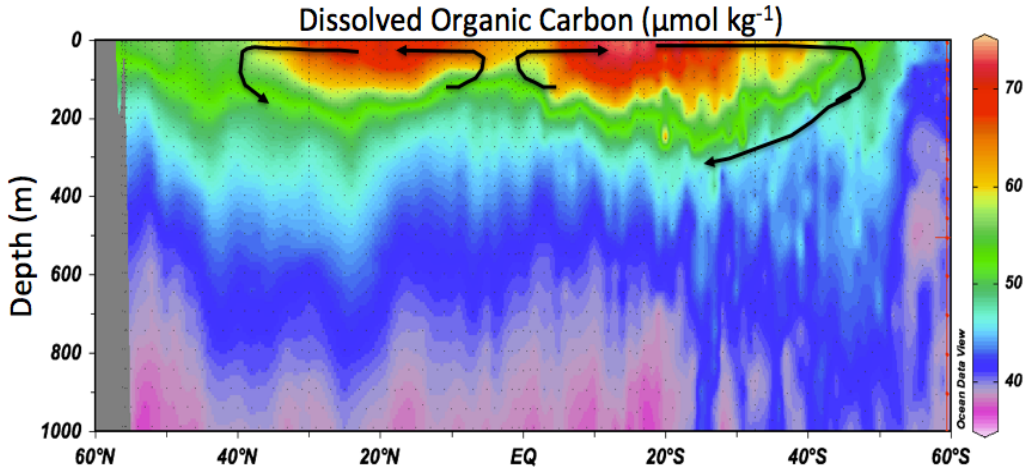

Figure 6. Distribution of DOC (µmol kg^{-1}) along P16 meridional transect (150° W) in the Pacific basins. This figure depicts accumulation DOC in the surface waters of the equatorial Pacific of which a portion is redistributed poleward by wind driven circulation. This horizontal export contributes to DOC build up in the subtropical gyres (PDW), which can then lead to vertical export into the interior via intermediate water formation. The arrows represent generalized water circulation. Data for this graph are available at http://ushydro.ucsd.edu/data_centers.htm.

3.0 Time-series of Biogeochemical Observations in the Equatorial Pacific

While the basin-scale understanding of biogeochemical processes is principally derived from repeat hydrographic cruises, our present understanding of the sea-air CO_2 flux in the equatorial Pacific is primarily derived from very high-quality surface carbon measurements on research cruises, volunteer observing ships and moorings coupled with satellite measurements of SST and winds from which flux algorithms have been derived (Cosca et al., 2003, Feely et al., 1999, 2002, 2006; Ishii et al., 2004, 2011, 2014; Takahashi et al., 2003, 2009; Wanninkhof et al., 2013; Figure 7). These data sets have been integrated into the community-wide data product Surface Ocean CO_2 Atlas (SOCAT; Pfeil et al., 2013; Bakker et al., 2014) and the Takahashi pCO_2 data product (Takahashi et al. 2013, CDIAC) for the tropical ocean and also have been used to validate models of carbon dioxide fluxes and variability over the last few decades (Doney et al., 2009; Le Quéré et al., 2009; Fay and McKinley, 2013). Two major conclusions have resulted from the synthesis and modeling research on the tropical and global data sets:

1. The tropical Pacific is the major natural source of CO_2 from the ocean to the atmosphere, contributing nearly 70% of the global flux to the atmosphere.
2. Interannual variability of the sea-air CO_2 flux in the tropical Pacific is also the major source of CO_2 flux variability in the global oceans (Doney et al., 2009; Ishii et al 2014). These two facts emphasize the strong need for sustained observations of carbon system parameters in this region.

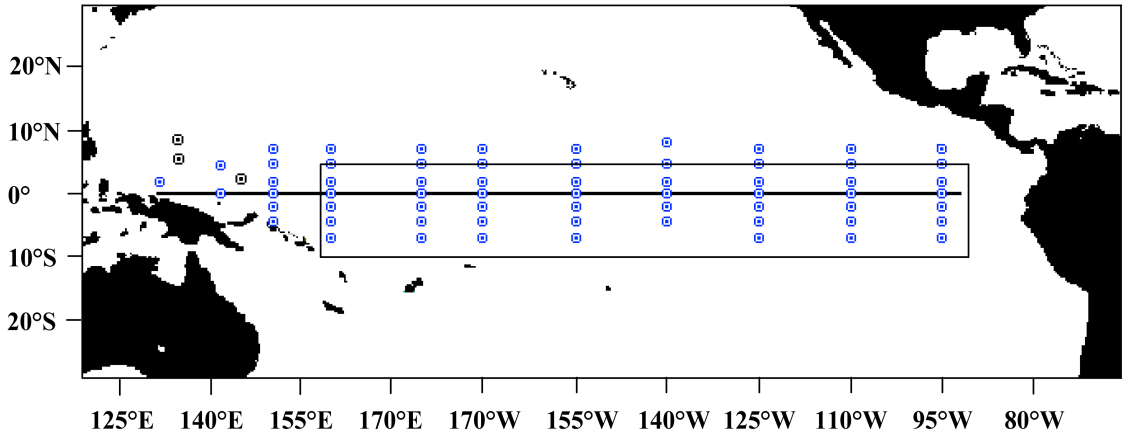

Figure 7. Locations of the TOA-Triton buoys. Moored pCO_2 data is collected mostly along the equator, shown as the dark line. Underway surface ocean pCO_2 measurements have been collected on surface ships as part of the bi-annual servicing of the TAO array.

4.0 Current and Emerging Technology

4.1 Underway Vessel Observations

Sea surface pCO_2 observations have been made on research vessels servicing the TAO/TRITON array since 1982. These automated underway systems are designed to continuously measure seawater and atmospheric pCO_2 onboard ships of opportunity with a high degree of precision (±0.5 µatm) and accuracy (±2 µatm). In this method, seawater is equilibrated with air in a chamber, dried, and pumped through a non-dispersive infrared (NDIR) analyzer. Each measurement is calibrated *in situ* against three or four gas reference standards certified by the World Meteorological Organization (WMO). Oxygen and nutrient sensors have not yet been integrated into the underway measurements made in the Tropical Pacific. These measurements are critically important in constraining the spatial variability of surface pCO_2 values. Accordingly, automated underway pCO_2 systems should be installed and maintained on all vessels servicing the TAO/TRITON array.

4.2 Moorings Observations

The ENSO observing system in the equatorial Pacific includes moored autonomous pCO_2 ($MAPCO_2$) systems deployed on 6 of the 7 flux reference sites along the equator (0°, 110°W; 0°, 125°W; 0°, 140°W; 0°, 155°W; 0°, 170°W; and 0°, 165°E) and a mooring in the warm water pool of the western equatorial Pacific (8°S, 165°E; Figure 7). The $MAPCO_2$ system collects marine boundary air and surface seawater xCO_2 (the mole

fraction of CO_2 in air in equilibrium with sea surface temperature) measurements every three hours and is similar to the underway method utilizing a pCO_2 equilibrator and Non-Dispersive Infra-Red (NDIR) analyzer. Each measurement is calibrated *in situ* against a WMO certified gas reference standard. Based on laboratory tests and field intercomparisons at PMEL and other institutions, estimates of uncertainty for air and seawater pCO_2 measurements are better than 1 and 2 µatm, respectively. The data from the $MAPCO_2$ systems have provided new insights (e.g. Sutton et al., 2014) into the seasonal cycles and the trends in annual CO_2 fluxes.

4.3 Repeat Hydrography Measurements

Ship-based hydrography is the only method for obtaining discrete high-quality carbon, oxygen, and nutrient measurements over the full water column and in areas of the ocean inaccessible to other platforms. Global hydrographic surveys have been carried out every decade since the 1980s through research programs such as GEOSECS, WOCE/JGOFS, CLIVAR and GO-SHIP. Repeat hydrographic lines that have crossed the TOA/TRITON array are: P13, P14, P15, P16, P17, and P18. During these cruises, observations of pCO_2 (ship's underway system) provide additional spatial context for the moored $MAPCO_2$ systems and discrete sampling of dissolved inorganic carbon (DIC) and total alkalinity (TA) are used to determine changes in water column carbon inventories, shoaling of the lysocline and provide insight into other biogeochemical processes.

Repeat measurements of limiting trace nutrients in the equatorial Pacific are required to better elucidate the role that they play in regulating primary productivity and carbon export in this broad region of the ocean. However, given the course spatial resolution and sparse temporal resolution, many questions still remain. Samples collected from *in situ* sampling devices placed on moorings would allow understanding of temporal variability in macro- and micronutrient supply (particulate and dissolved) within the EUC and would thus help constrain the effects of short term variability in the supply as both a throttle on primary productivity and on net productivity in the eastern tropical Pacific. The use of nitrate sensors on autonomous vehicles would identify regions where macronutrients are readily available and thus areas where primary productivity is likely limited by Fe and/or other trace nutrient metals. Long-term records over significant spatial scales would aid in targeting regions for more extensive, ship-based studies, aimed at understanding this process. Establishing an area for ship-based time series studies will be essential if we are to fully understand the physical and chemical forcing on primary productivity and carbon export.

In the future, improved understanding of the distribution and magnitude of source waters to the EUC and their geochemical make-up will be essential. This information will aid in constraining whether longer-term shifts in primary productivity are the result of longer-term shifts in the geo-chemical make-up of the source waters. A fuller geochemical examination of this region will be required to accomplish this.

4.4 Satellites Observations

While it is not possible to measure surface ocean pCO_2 from satellite, estimates of phytoplankton biomass and primary productivity have been made continuously from August 1997 by SeaWiFS, MODIS and other satellite ocean color missions. These observations have proved essential for filling in gaps between ship and mooring data, and Chavez et al (1999) showed excellent agreement for chlorophyll observations across all three platforms. Recent work (Hales et al, 2012) has demonstrated the use of multiple satellite-measured parameters for estimating surface ocean pCO_2, as did Cosca et al. (2003) for *in situ* measurements. Because of the strong relationship between upwelling (and its SST signature), productivity and pCO_2, the equatorial Pacific is a region that holds promise for future work linking pCO_2 to satellite observations. Continued observations of surface pCO_2 from moorings and vessel underway systems will allow for further improvement of the empirical relationships between SST and salinity, which will be necessary for satellite pCO_2 algorithm development.

5.0 Potential Expansion of CO_2 and Biogeochemical Measurements

The autonomous carbon sensors described in sections 4.1.1 and 4.1.2 provide climate quality (uncertainty < 2 μatm) seawater pCO_2 measurements. However, since these instruments were developed to measure sea-air flux, they can only be operated at the ocean surface and are not adaptable to subsurface drifters or gliders. There has been some success in developing algorithms to predict ocean acidification parameters in coastal environments using temperature, salinity, and oxygen, which can be measured on subsurface platforms, but these algorithms are not reliable in surface waters largely due to heat and oxygen fluxes to the atmosphere that do not have an associated carbon signature (Juranek et al. 2009, 2011; Alin et al. 2012). The algorithms developed by Feely et al. (2006) to predict seawater pCO_2 based on SST and SSS are robust, but must be validated using underway-data with sufficient spatial (i.e., spanning the Tropical Pacific) and temporal resolution (i.e., capturing seasonal and ENSO variability). These surface seawater pCO_2 algorithms must be recalculated every 5-10 years in order to reevaluate the influence of changing atmospheric CO_2 on the surface ocean. These facts clearly demonstrate the need for continued direct observations of the carbon parameters as well as underlying biogeochemistry. However, as ship-time becomes more costly, it will be necessary to develop more robust, reliable and accurate autonomous sensors and platforms.

5.1 Experiments and Pilot Studies Necessary For New Observations

One of the most promising new technologies that could supplement existing platforms and perhaps reduce some of ship-time needs is the carbon wave glider (Figure 8). This platform is designed to conduct autonomous, basin-scale ocean transits for long-durations (up to 6 months). The wave glider has to date been tested extensively in coastal environments with pCO_2, pH, and nitrate sensors at the surface and temperature and oxygen at 6 m depth on the subsurface, energy-harvesting vanes. Because the $MAPCO_2$ systems that are used on the moorings have been integrated into the wave gliders is it possible for them to return the same climate-quality pCO_2 data and provide data inter-comparison with the moorings and underway *p*CO2 measurements from vessels. In order to assess the carbon wave glider in a high energy, open ocean environment, a 3-6 month

pilot-study experiment in the equatorial Pacific is necessary. Comparison to proven technology and standardized methods (i.e., underway pCO_2, mooring pCO_2, and bottle samples) should be used to validate the wave glider carbon system and biogeochemical sensors. Accordingly, this pilot-study should be done in conjunction with either a repeat hydrography cruise or a mooring servicing cruise where underway and discrete measurements can be made. In the future, faster autonomous platforms that have larger payloads such as the Sail Drone should be adapted to make pCO_2 and related biogeochemical measurements. These drones can cover larger areas of the ocean and carry more sensors with greater endurance.

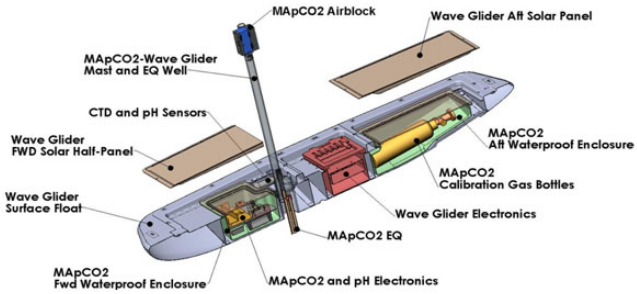

Figure 8 – Carbon wave glider with integrated MAPCO$_2$ system.

A more robust and immediate capability that should be added to the existing mooring array and vessel-mounted underway systems operating in the region are autonomous sensors for dissolved oxygen and inorganic nitrate. In both cases, existing sensor technology has reached the stage where continuous measurements can be made with high precision during a 12-month deployment period. The addition of these new sensors would provide valuable insights into the seasonal nutrient delivery into the mixed layer and give an indication of the intensity and duration of primary production. Other "off-the-shelf" technologies that could greatly supplement the existing mooring array are the remote access sampler (RAS) and sediment traps. The RAS has the ability to collect 96 (8 per month) discrete water samples at fixed depths. The data could be used to calibrate moored sensors as well as provide increased temporal resolution for parameters such as Fe, silicate and DOM, which can't be measured autonomously. Sediment traps can also provide discrete estimates of particles fluxes out of the surface ocean and are important indicators of primary production that can be related to satellite data.

Finally, a significant effort should be made to outfit ARGO floats with biogeochemical sensors. At present, the only biogeochemical sensors that have been tested on these platforms are dissolved oxygen and pH. While both have been limited by hysteresis effects and calibration issues, the performance and reliability of these sensors is improving. Further efforts should be made to incorporate other measurements, particularly nitrate into these sensor packages. Additionally, Slocum gliders that can

profile the water column provide another autonomous platform where oxygen, nitrate and pH sensors can be incorporated. While an order of magnitude more expensive than an ARGO float, the Slocum's can carry a greater payload and have some navigation capability. Another emerging sensor package is the Carbon Prawler that integrates carbon and biogeochemical measurements. These systems can be deployed on a mooring and by moving up and down the wire can profile the water column. The Prawler's can also be deployed on CTD casts during repeat hydrography cruises and provide high-resolution profiles of the water column. When properly integrated, the combination of moorings, underway ship-based observations, repeat hydrographic measurements, gliders, floats, RAS, and satellite data streams can provide a four-dimensional picture of carbon biogeochemistry in the equatorial Pacific Ocean.

6.0 Recommendations for TPOS 2020

Based upon the discussion within this White Paper, we make the following overall recommendation for the TPOS of 2020:

1. Long climate and pCO_2 records should be continued at the existing TAO/TRITON locations.
2. The research vessels that are used to maintain the observing system should be treated as a platform within the observing system itself, making standard measurements along repeat tracks (e.g. CTD, pCO_2, dissolved oxygen, nitrate, pH, etc.) and deployment of moorings, floats and gliders.
3. The TPOS array should integrate multi-disciplinary observations. Data should be freely provided for all users. The array should be designed to provide data needed to observe ENSO events through their full life cycle; to force, initialize, and validate numerical models; to assess uncertainties in numerical models and satellite products; to calibrate remotely measured variables; to develop and test parameterizations needed for models and satellite products; and to better understand the climate system.
4. Interdisciplinary process and pilot studies should be built around the infrastructure of the TPOS. New platforms such as wave gliders, remote access water samplers, and sediment traps should be added to the existing array and new sensors (e.g. pCO_2, pH, dissolved oxygen, nitrate, pH, etc.) should be added to existing assets.

7.0 Conclusion Statement

Decades of work and millions of observations have shown that the tropical Pacific is the major natural source of CO_2 from the ocean, contributing nearly 70% of the global flux to the atmosphere. Data synthesis and modeling efforts have confirmed that interannual variability of the sea-air CO_2 flux in the tropical Pacific is the major source of CO_2 flux variability in the global oceans. Much of the CO_2 flux is controlled by the underlying physical and biogeochemical processes in the region, which are impacted by decadal and longer time-scale ocean and climate processes. Given its role in global climate and potential impacts to ocean resources and billions of people around the world the TPOS must be maintained at a level commensurate with its importance.

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