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# Rain impacts on $CO_2$ exchange in the western equatorial Pacific Ocean

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[1] The ocean plays a major role in the global carbon cycle through the atmosphere-ocean partitioning of atmospheric carbon dioxide. Rain alters the physics and carbon chemistry at the ocean surface to increase the amount of $CO_2$ taken up by the ocean. This paper presents the results of a preliminary study wherein rain measurements in the western equatorial Pacific are used to determine the enhanced transfer, chemical dilution and deposition effects of rain on air-sea $CO_2$ exchange. Including these processes, the western equatorial Pacific $CO_2$ flux is modified from an ocean source of +0.019 mol $CO_2$ $m^{-2}$ $yr^{-1}$ to an ocean sink of −0.078 mol $CO_2$ $m^{-2}$ $yr^{-1}$. This new understanding of rain effects changes the ocean's role in the global carbon budget, particularly in regions with low winds and high precipitation. **Citation:** Turk, D., C. J. Zappa, C. S. Meinen, J. R. Christian, D. T. Ho, A. G. Dickson, and W. R. McGillis (2010), Rain impacts on $CO_2$ exchange in the western equatorial Pacific Ocean, *Geophys. Res. Lett.*, *37*, L23610, doi:10.1029/2010GL045520.

## 1. Introduction

[2] Wind is one of the important factors that control air-sea gas exchange over the ocean, but other environmental processes such as rain may play a significant role in the exchange of $CO_2$ between the ocean and atmosphere. Rain induces surface layer chemical dilution, enhances the gas transfer velocity and exports carbon from the atmosphere by wet deposition. However, regional and global bulk estimates of air-sea $CO_2$ flux have to date mostly ignored these effects [*Feely et al.*, 2006; *Ishii et al.*, 2004; *Takahashi et al.*, 2002]. Rain effects are likely to be particularly important in tropical areas, such as the western equatorial Pacific (WEP), where low wind speeds are often observed in concert with high precipitation.

[3] Sea surface chemical dilution by rain is a well-known process that reduces near-surface salinity, total alkalinity (TA), and dissolved inorganic carbon (DIC) in proportion to the excess of precipitation over evaporation. This dilution decreases $p(CO_2)$ in the surface boundary layer [*Dickson et al.*, 2007]. While ocean surface mixing will normally homogenize any surface chemical change, a surface effect can be maintained for a significant time during rain in low wind conditions.

[4] There is also an enhanced transfer velocity due to rain-induced surface turbulence [*Ho et al.*, 1997, 2000, 2004; *Takagaki and Komori*, 2007; *Zappa et al.*, 2007, 2009], significantly altering the air-sea $CO_2$ flux. In high precipitation regions where the wind speed is typically low, it is conceivable that the rain effect may be of comparable magnitude to the wind effect. As rain increases the transfer velocity and decreases surface water $pCO_2$ due to chemical dilution, the net effect may differ between ocean $CO_2$ sink regions (where ocean $pCO_2$ is lower than atmospheric) and ocean source regions. In ocean sink regions, rain would enhance the sink. In ocean source regions, however, it will depend on which rain effect (enhanced gas exchange or reduced ocean $pCO_2$) dominates. An additional precipitation effect results from wet deposition of DIC [*Komori et al.*, 2007] and dissolved organic carbon (DOC) in rainwater [*Willey et al.*, 2000] to the ocean surface. It is therefore critical for these rain influences to be studied together.

[5] The WEP has been shown to have $pCO_2$ 10–30 $\mu$atm above atmospheric [*Ishii et al.*, 2004] and a small exchange of $CO_2$ with the atmosphere. Including only wind effects, the estimated fluxes are 0.07–0.25 mol $m^{-2}$ $y^{-1}$ [*Feely et al.*, 2006; *Ishii and Inoue*, 1995; *Ishii et al.*, 2004]. Due to its high precipitation [*Feely et al.*, 2002], generally low winds, and large area, the WEP is ideal to study the combined effects of rain on $CO_2$ flux.

[6] There have been no studies to date that have considered the combined effect of rain influences on surface salinity, gas transfer velocity, wet deposition, and surface $pCO_2$. Rain effects are still mostly neglected in estimates of air-sea gas exchange. Here, we use *in situ* precipitation measurements from the Tropical Atmosphere Ocean (TAO) buoy at 0°, 156°E (http://www.pmel.noaa.gov/tao/) during 2002, a dilution model based on observational Biosphere 2 ocean studies, and output from an ocean carbon cycle model to predict for the first time the effects of rain on the air-sea carbon flux in the WEP.

## 2. Data and Methods

[7] Air-sea flux of $CO_2$ due to wind, $F_{wind}$, is estimated as $F_{wind} = k_{wind}\,\alpha\,(p(CO_2)_{water} - p(CO_2)_{air})$, where $k_{wind}$ is the

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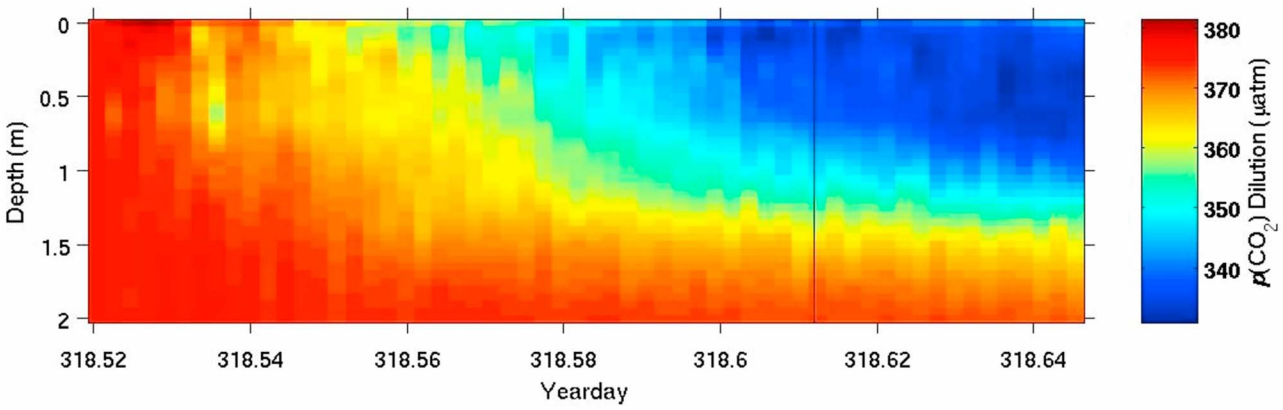


**Figure 1.** Evolution of near-surface $p(CO_2)$ during a precipitation event as determined in Biosphere 2 ocean seawater experiments. Rain stratifies, mixes and dilutes the ocean water in this Biosphere 2 ocean experiment to a depth of $O$(10cm). As surface dilution is increased, salinity, DIC, and TA decrease, and $p(CO_2)$ is reduced from its initial, ambient pressure.

gas transfer velocity due to wind, $\alpha$ is the solubility of $CO_2$ in seawater and $p(CO_2)_{air}$ and $p(CO_2)_{water}$ are the partial pressures of $CO_2$ in air and surface seawater respectively. The transfer velocity is determined using the quadratic parameterization of *Wanninkhof* [1992] and the time series of wind speed at 156°E, 0°N. The results shown are not particularly sensitive to the choice of $k_{wind}$ parameterization. Values of $p(CO_2)_{air}$ and $p(CO_2)_{water}$ are taken from the ocean carbon cycle model simulation [*Christian et al.*, 2008].

[8] The air-sea flux due to rain-enhanced transfer velocity (but not other effects of rain) is given by $F_{rain\text{-}k} = k_{total}\ \alpha\ (p(CO_2)_{water} - p(CO_2)_{air})$ where $k_{total}$ is the total transfer velocity due to wind and rain expressed as the sum of $k_{wind}$ and the transfer velocity due to the precipitation, $k_{rain}$, estimated using the parameterization based on rain rate [*Ho et al.*, 1997] and rain measurements from the TAO buoy at 156°E, 0°N. We assume that the effects of wind and rain on interfacial turbulence are linearly independent and therefore additive at low wind speeds [*Ho et al.*, 2007].

[9] The combined processes of enhanced transfer velocity and of chemical dilution of surface water $p(CO_2)$ during rain give the air-sea flux during rain events, $F_{interfacial} = k_{total}\ \alpha\ (p(CO_2)_{dilution} - p(CO_2)_{air})$, where $p(CO_2)_{dilution}$ is the ocean surface $p(CO_2)$ after chemical dilution. Because it is confined to a thin surface layer, the dilution effect cannot be resolved in standard surface mixed-layer models and must be parameterized along with the gas transfer velocity. The dilution model developed from the observational Biosphere 2 ocean studies [*Zappa et al.*, 2009] is applied to the salinity and rain time series from the TAO buoy at 0°, 156°E to determine the sea surface salinity dilution. The observational data from the Biosphere 2 ocean studies [*Zappa et al.*, 2009] showed a rate of sea surface salinity (SSS) dilution that is linearly dependent on the measured rain rate. For each time step of one hour using the TAO buoy data, SSS is diluted at a rate prescribed by the measured rain rate. This volumetric dilution of the SSS acts as a tracer for fresh rainwater input and determines the DIC and alkalinity dilution. Following the rain, the surface is mixed back to the climatological state instantaneously. If there was no rain, the original surface SSS value was retained. During rain events, a small amount of DIC (13 $\mu$M) and an insignificant amount of TA is added to the surface ocean by the rain. Effects of dilution of DIC and TA on $p(CO_2)_{water}$ are determined based on standard carbon system models [*Dickson et al.*, 2007] to give $p(CO_2)_{dilution}$.

[10] In this study we use the rain parameterization from laboratory experiments in freshwater. Laboratory experiments in saltwater indicate that rain-induced $k$ is similar to that predicted from the relationship established using freshwater laboratory experiments [*Zappa et al.*, 2009]. While it was shown that the increased surface turbulence due to rain (i.e., surface mixing) caused a substantial increase in the transfer velocity, a near-surface stratified layer developed that trapped this mixing very near the surface ($O$(10 cm)). Because vertical mixing is inhibited by the near-surface stratification and does not allow for the replenishment of gas in this surface layer, the surface chemical dilution described here may be prolonged and have an even more pronounced effect.

[11] *Henocq et al.* [2010] estimate the effect of rain events on vertical salinity gradients in the top 10 m of the ocean surface layer using TAO mooring measurements. Their results show that salinity measurements at 5 and 10 m depth often do not capture the salinity dilution during rain events detected by measurement at 1m depth. Furthermore, the SSS dilution observed at 1 m by *Henocq et al.* [2010] is comparable to the measurements of SSS dilution in the Biosphere 2 ocean studies and to the modeled SSS dilution results presented here using the TAO buoy data.

[12] The wet deposition flux of DIC, $F_{DIC}$, is estimated as $F_{DIC} = R_n\ \alpha\ p(CO_2)_{air}$, where $R_n$ is the rain rate in mm $h^{-1}$ [*Komori et al.*, 2007]. This is based on the assumption that the raindrops are in equilibrium with the atmosphere when they reach the ocean [*Sugioka and Komori*, 2007]. Therefore, the total $CO_2$ flux due to rain is $F_{rain} = F_{interfacial} + F_{DIC}$. Inclusion of the chemical dilution and rain gas transfer velocity terms as well as wet deposition can result in a non-zero $CO_2$ flux even at zero wind and with ocean and atmosphere initially at equilibrium.

## 3. Results and Discussion

[13] Figure 1 shows the effect of rain water chemical dilution during the observational Biosphere 2 ocean studies.

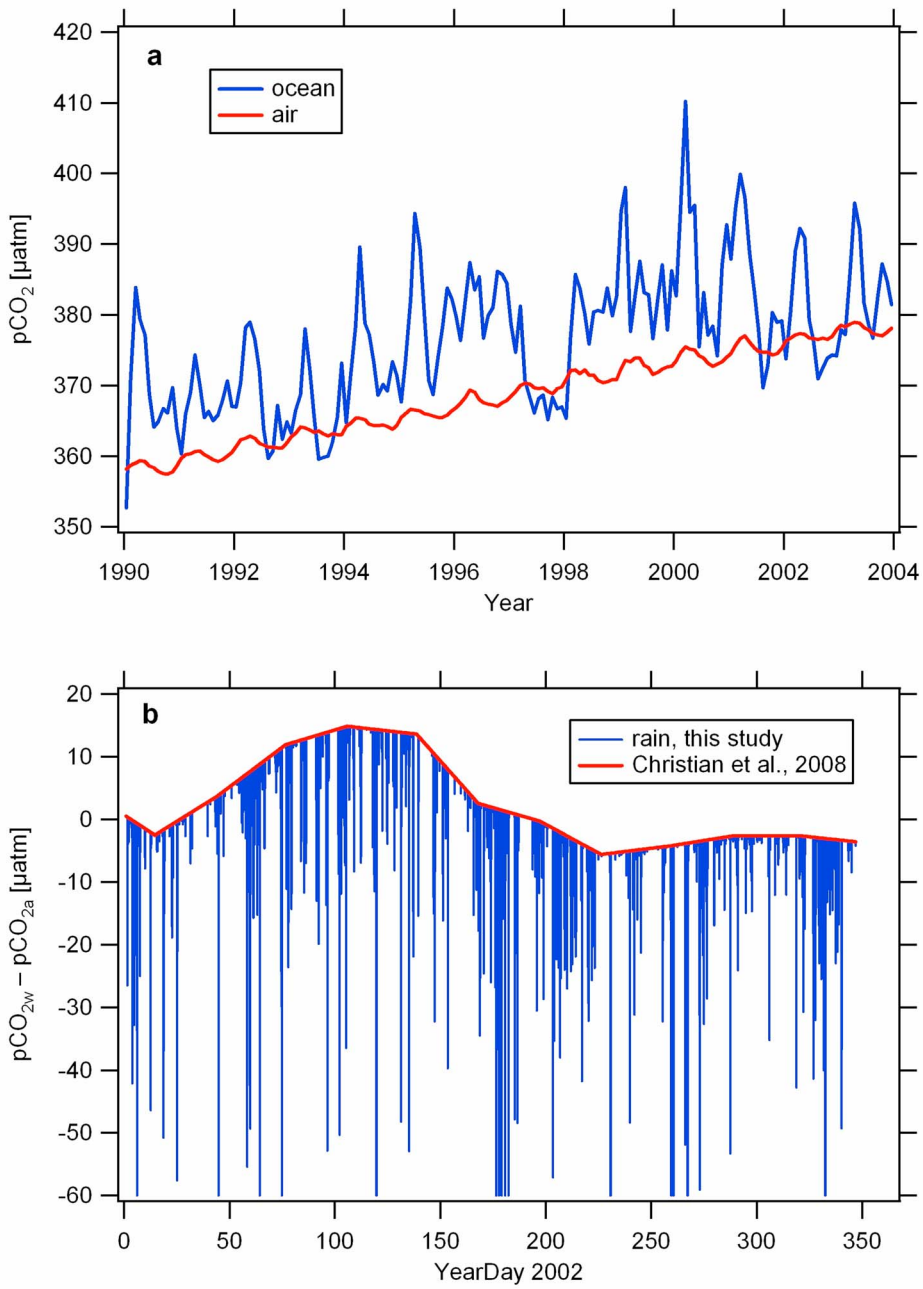


**Figure 2.** (a) Surface ocean $p(CO_2)$ variations over multiple years at 156°E, 0°N from *Christian et al.* [2008], and (b) the $p(CO_2)$ for 2002 determined in this study including the rain chemical dilution.

In less than an hour of rain, surface ocean $pCO_2$ drops more than 30 $\mu$atm. This happens in a surface layer less than 1 m thick, which is not resolved by most models. The rain rate and background near-surface mixing define the penetration depth of the rain dilution. The dilution model assumes that the background mixing is similar to that measured during the Biosphere 2 ocean experiments. Measurements of the background turbulent kinetic energy dissipation rate in the Biosphere 2 ocean studies were $O(10^{-5}$ to $10^{-4}$ W kg$^{-1})$ [*Zappa et al.*, 2009]. This is more energetic than what is common for the mixed layer in the equatorial Pacific $O(10^{-7}$ to $10^{-6}$ W kg$^{-1})$ [*Wijesekera and Gregg*, 1996]. Therefore, the chemical dilution used in this study may underestimate the actual dilution and serves as a conservative value determining the effect in the WEP region.

[14] Figure 2a shows ocean surface $pCO_2$ at 0°, 156°E from an ocean carbon cycle model simulation [*Christian et al.*, 2008]. The overall trend follows the atmospheric increase with seasonal and interannual variations. Surface chemical dilution is included as outlined above using the results of the observational Biosphere 2 ocean experiment (Figure 1). The rain events during 2002 decrease the surface ocean $pCO_2$ by more than 30 $\mu$atm and by up to 60 $\mu$atm for the highest rain rates compared to the bulk mixed layer value used in the simulation (Figure 2b). The year 2002 was chosen since the data for this year was the most complete and the

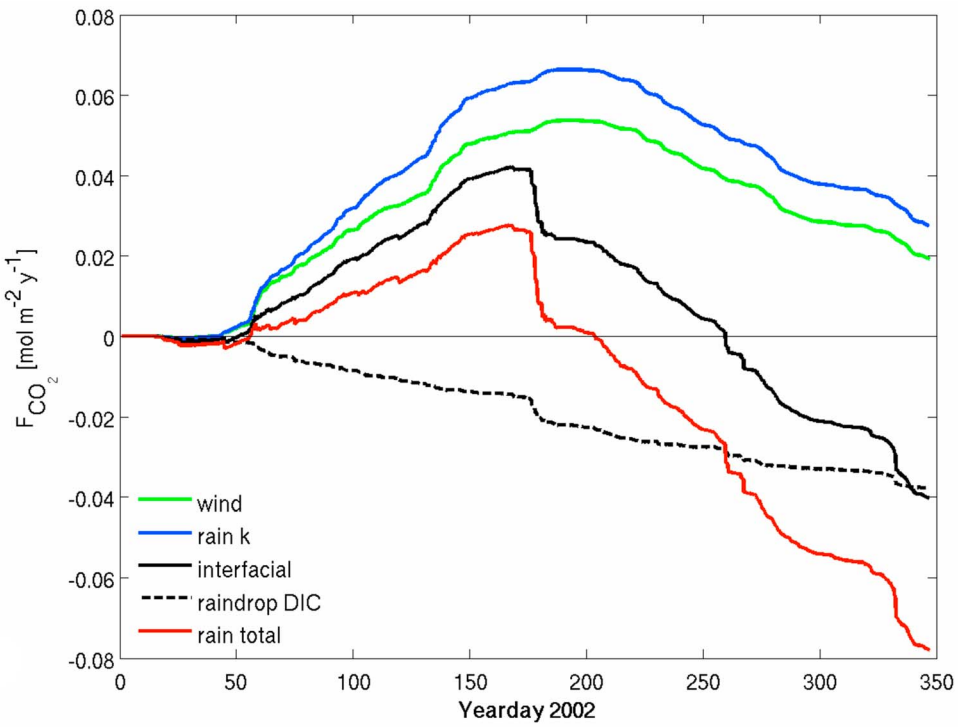


**Figure 3.** Cumulative net air-sea $CO_2$ fluxes during 2002 at 156°E at the equator. Flux from ambient $p(CO_2)$ climatology and wind only gas transfer velocity (green), from ambient $p(CO_2)$ and rain gas transfer velocity (blue), from $p(CO_2)$ chemical dilution and rain gas transfer velocity, or interfacial flux (black solid), from raindrop wet deposition of DIC (black dash), and from the total rain (red).

ocean transitions from a $CO_2$ source to a sink. The rain rate and wind speed distributions for years 2000–2008 from the TAO buoy at 156°E, 0°N show modest differences from year to year and thus the year 2002 can be considered representative of the years before and after (see Figures S1a and S1b of the auxiliary material).[1]

[15] Gas transfer velocities calculated from TAO buoy data at 156°E, 0°N show that $k_{total}$ increased on average by 9% compared to $k_{wind}$. The transfer velocity associated with rainfall increases with rain rate, reaching a maximum value of just over 50 cm h$^{-1}$ at the highest observed rainfall rate of 108 mm h$^{-1}$. Of course, the impact of increasing wind speed quickly grows to even larger values of transfer velocity near 70 cm h$^{-1}$ for the maximum values of wind speed near 15 m s$^{-1}$ observed at the mooring. A central issue is the relative importance of the rainfall-induced gas exchange, chemical dilution and deposition for tropical open ocean conditions of wind speed and rainfall.

[16] Analysis of the magnitudes of the various rain terms shows that the interfacial transfer effects, including chemical dilution and enhanced transfer velocity, and wet deposition effects on the WEP $CO_2$ gas flux are significant relative to wind (Figure 3). In early 2002, the net air-sea fluxes are initially positive because the ocean $pCO_2$ is supersaturated. For this period, the flux considering the rain-enhanced gas transfer velocity, $F_{rain\text{-}k}$, is greater than that of wind only, $F_{wind}$, because of the enhanced gas transfer velocity due to rain-induced surface turbulence applied to an undiluted surface ocean $pCO_2$. The flux that includes both the effects of enhanced gas transfer due to rain and chemical dilution due to rain, $F_{interfacial}$, is lower than $F_{rain\text{-}k}$ because the chemical dilution reduces the surface ocean supersaturation. Around yearday 200 the ocean-atmosphere $p(CO_2)$ difference becomes negative and the ocean becomes a net $CO_2$ sink. The cumulative $F_{wind}$ and $F_{rain\text{-}k}$ remain positive, however. Without consideration of the dilution effect, the ocean would mistakenly be considered a net $CO_2$ source over the year. The wet deposition flux, $F_{DIC}$, also contributes significantly to the ocean carbon sink. For the combination of all the rain effects as defined by the total carbon dioxide flux due to rain, the ocean becomes a significant sink for $CO_2$. The total yearly $CO_2$ flux, $F_{rain}$ [mol m$^2$ yr$^{-1}$], due to rain including enhanced gas transfer, chemical dilution, and wet deposition, is into the ocean with a net flux approximately four times larger, and of opposite sign, than would be determined using wind-only or rain gas transfer-only fluxes.

[17] The individual components of the yearly cumulative $CO_2$ flux due to rain in 2002 at 0°, 156°E, are summarized in Table 1. The yearly cumulative $CO_2$ flux due to wind

**Table 1.** The Air-Sea $CO_2$ Flux Components for Year 2002 at 156°E, 0°N

| Component | Flux [mol m$^{-2}$ yr$^{-1}$] | Variable |
|---|---|---|
| Rain | | |
| Dilution and Rain $k$ | −0.040 ± 0.012 | $F_{interfacial}$ |
| DIC Wet deposition | −0.038 ± 0.001 | $F_{DIC}$ |
| Rain Total | −0.078 ± 0.013 | $F_{rain}$ |
| Wind | 0.019 | $F_{wind}$ |

[1] Auxiliary materials are available in the HTML. doi:10.1029/2010GL045520.

alone is also shown. The net flux of $CO_2$ due to chemical dilution and rain transfer velocity effects was $-0.040 \pm 0.012$ mol $m^{-2}$ $yr^{-1}$, and the net flux of $CO_2$ due to wet deposition for DIC was $-0.038 \pm 0.001$ mol $m^{-2}$ $yr^{-1}$. By including these effects of rain, the estimated WEP flux of $CO_2$ changes from being an ocean source to the atmosphere of +0.019 mol $m^{-2}$ $yr^{-1}$ to an ocean sink from the atmosphere of $-0.078 \pm 0.013$ mol $m^{-2}$ $yr^{-1}$ in 2002. Assuming the model accounts for all important processes, the uncertainty in the computed fluxes is due to the uncertainty of the dilution rate model coefficients and a 5% uncertainty in the measured rain rate on the buoys.

[18] The extent of the large-scale spatial variability of wind and rain affects whether these results are representative for the wider equatorial region. We have compared the distributions of both wind speed and rain rate at 156°E to those at the other longitudes along the equator from 147°E to 110°W using all TAO buoy data available from 1997 through 2009. The rain rate distributions at two other sites in the WEP (147°E and 165°E, the latter of which is on the edge of the WEP) are essentially the same as at 156°E (Figures S2a and S2b). Moving eastward into the central (CEP) and eastern (EEP) equatorial Pacific, rainfall gradually declines in magnitude and frequency. The distributions of wind speed at 147°E and 156°E are essentially the same. East of 165°E, the wind distributions narrow and the peaks shift from around 3–4 m $s^{-1}$ to around 5–7 m $s^{-1}$. Therefore, the spatial variability observed in the TAO array does not preclude the extension of our results to the broader WEP.

[19] Rain effects are modeled here only during rain events. However, previous studies based on TAO salinity and rain rate observations [*Henocq et al.*, 2010] have shown that the salinity dilution can persist for several days. The geographical extent of a rain event rarely exceeds 200 km × 200 km, yet mixing and ocean surface currents can spread freshwater over a larger area. The thickness of this rain-induced surface layer is important to the interpretation of the rain-induced dilution effects discussed here. For example, while rain patterns will tend to create a fresh layer on the surface over a large horizontal area, the possibility of further spreading and thinning of the rain-induced surface layer may decrease the air-water $pCO_2$ difference. These effects will require additional study to determine the application of the results of this preliminary analysis to the overall exchange of $CO_2$ across the tropical ocean surface.

## 4. Conclusions

[20] Rain may have a significant effect on air-sea $CO_2$ exchange directly through increased transfer velocity and indirectly by chemical dilution and wet deposition. Particularly in regions of low wind and high precipitation, such as the WEP region, these processes must be considered for estimation of air-sea $CO_2$ flux. The results of this pilot investigation show that during high rainfall events, chemical dilution from the rain can lower the surface ocean $pCO_2$ in these regions by more than 30 $\mu$atm. This increases the air-sea $\Delta pCO_2$ in ocean sink regions, while in ocean source regions $\Delta pCO_2$ is lowered and can potentially turn a weak source into a sink. As this effect is confined to a very near-surface layer it is neglected in surface mixed layer and climate models as well as by standard measurements of surface $pCO_2$ that are normally made at 3–5 m depth. Rain also increases the gas transfer velocity, further enhancing the sink potential. In this study, precipitation results in a $CO_2$ sink of $-0.078 \pm 0.013$ mol $m^{-2}$ $yr^{-1}$ where the global average flux is less than $-0.35$ mol $m^{-2}$ $yr^{-1}$ making chemical dilution, enhanced gas transfer, and wet deposition significant contributions to the ocean $CO_2$ sink. Consideration of these physical and biogeochemical factors changes the ocean's role in the global carbon budget, particularly in regions with low winds and high precipitation. Given the fact that low-wind, high-precipitation conditions dominate most of the tropical regions around the globe, encompassing roughly five percent of the total earth surface area, incorporating this new carbon-exchange precipitation mechanism discussed herein into future global carbon budgets will be critical for identification of important interannual and decadal climate signals.

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