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A 1-D examination of decadal air–sea re-equilibration induced ocean surface anthropogenic CO$_2$ accumulation: present status, changes from 1960s to 2000s, and future scenarios

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Abstract

Based upon the well-understood carbonate system chemistry over global ocean surface (above the wintertime thermocline and shallower than upper 100 m), we investigated potentials of wintertime ocean surface DIC (dissolved inorganic carbon) to rise in response to the decadal air–sea re-equilibration, and the corresponding anthropogenic CO$_2$ accumulation rates. For a reference year 2000, the potentials of wintertime DIC to rise in response to the rising atmospheric CO$_2$ mole fraction ranged from 0.28 to 0.70 µmol kg^{-1} ppm^{-1} (ppm = parts of CO$_2$ per million dry air) over the global open ocean surface, while the global mean wintertime surface DIC increase rate was close to 1.0 µmol kg^{-1} yr^{-1}. The decadal anthropogenic CO$_2$ accumulation rate within the surface ocean was estimated at 0.31 × 10^{15} g C yr^{-1} around the reference year 2000, accounting for a non-negligible component (likely 12 to 14 %) of the recent oceanic sink for anthropogenic CO$_2$. From 1960s to 2000s, this rate likely increased by 47 % due to the accelerated atmospheric CO$_2$ rise. However, the ocean surface anthropogenic CO$_2$ accumulation potential under a unit atmospheric CO$_2$ rise may have declined by 16 % during the same period.

1 Introduction

Since the beginning of the industrial period in the late 18th century, large quantities of anthropogenic carbon dioxide (CO$_2$, a greenhouse gas species) were emitted to the atmosphere, from fossil fuel combustion, cement production, and land use change (Le Quéré et al., 2013). Although global oceans have absorbed ∼ 48 % of the total anthropogenic CO$_2$ emissions (Sabine et al., 2004), and net global carbon uptake by combined land and ocean carbon reservoirs has increased from 2.4 ± 0.8 Pg C yr^{-1} (Pg = 10^{15} grams) in 1960s to 5.0 ± 0.9 Pg C yr^{-1} in 2000s (Ballantyne et al., 2012), atmospheric CO$_2$ concentration (xCO$_2^{\text{air}}$, mole fraction in dry air) rises from a preindustrial value of 280 ppm (parts per million) to a present day value of 390 ppm

(WMO/GAW, 2012). Based on the Mauna Loa station data released by NOAA/ESRL at http://www.esrl.noaa.gov/gmd/ccgg/trends/, the decadal increase rates of atmospheric CO_2 concentration ($\delta x CO_2^{air}$) also rise from relatively low rates of 0.8 ± 0.4 ppm yr^{-1} in 1960s and 1.2 ± 0.6 ppm yr^{-1} in 1970s to moderate rates of 1.6 ± 0.4 ppm yr^{-1} in 1980s and 1.5 ± 0.7 ppm yr^{-1} in 1990s, and to a quite high rate of 1.9 ± 0.4 ppm yr^{-1} in 2000s.

Nowadays our understanding of natural carbon sinks and sources for atmospheric CO_2 is still insufficient to derive precise information for closing global carbon budget and thereby predicting the climate change. Identifying the mechanisms and locations responsible for the global carbon budget remains a huge challenge (Ballantyne et al., 2012). The surface ocean uptake of anthropogenic CO_2 is just the case.

The surface ocean, located above the wintertime thermocline and shallower than upper 100 m, is in direct contact with the atmosphere. It is expected to regain dynamic equilibrium with the rising atmospheric CO_2 quickly (Revelle and Suess, 1957; Oeschger et al., 1975; Broecker et al., 1979; Sundquist et al., 1979; Sundquist and Plummer, 1981; Brewer, 1983; Wallace, 2001), with the mixed layer DIC residence time of ~ 5 years as adopted by Craig (1957) and Bolin and Eriksson (1959). As a result, a small but solid increase in concentration of dissolved inorganic carbon (DIC) has been detected in the ocean surface in response to the atmospheric CO_2 rise (Winn et al., 1998; Gruber et al., 2002; Takahashi et al., 2003; Keeling et al., 2004; Bates et al., 2012).

This effect, chemical buffering capacity, has been traditionally characterized by Revelle factor (RF), i.e. the ratio of fractional change in seawater partial pressure of CO_2 (pCO_2) to the fractional change in DIC after re-equilibration (Revelle and Suess, 1957; Broecker et al., 1979; Sundquist et al., 1979; Li et al., 2001; Zeebe and Wolf-Gladrow, 2001; Denman et al., 2007). In the context of the oceanic mitigation of atmospheric CO_2 rise, the air–sea re-equilibration induced ocean surface anthropogenic CO_2 accumulation (R_{equ}) works to store the anthropogenic CO_2 in the ocean surface in decadal time scales, i.e. twice or several times the global mean residence time of ocean surface DIC. Based on this well-understood carbonate system chemistry over global ocean sur-

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face, a simple method for estimating R_{equ} under constant total alkalinity (TAlk) field has been proposed by Sundquist and Plummer (1981). However, they do not finish the assessment due to the insufficient knowledge about TAlk distributions and vertical mixing within the ocean surface until 1990s.

5 Recently, using oceanic inorganic carbon measurements from international survey efforts and tracer-based separation techniques, the oceanic uptake rate of anthropogenic CO_2 has been constrained to $2.2 \pm 0.4 \, \text{Pg C yr}^{-1}$ in 1990s (Denman et al., 2007), $2.3 \pm 0.6 \, \text{Pg C yr}^{-1}$ in 2000s (Khatiwala et al., 2009), and $2.5 \pm 0.5 \, \text{Pg C yr}^{-1}$ for the period from 2002 to 2011 (Le Quéré et al., 2013). However, how does R_{equ} con-

10 tribute to the present atmospheric CO_2 rise mitigation? So far this question is still unclear, although we know that the ocean surface anthropogenic CO_2 accumulation has reduced pH and carbonate ion concentrations in the ocean surface (e.g. Caldeira and Wickett, 2003; Sabine et al., 2004; Doney et al., 2009a; Byrne et al., 2010; Bates et al., 2012; Feely et al., 2012; Lauvset and Gruber, 2014), leading to ocean acidification.

15 Based on earlier simplified deduction and limited observation, a sea surface DIC increasing rate (δ DIC) in response to the rising atmospheric CO_2 had been suggested at a level of $1.0 \, \mu\text{mol kg}^{-1} \text{yr}^{-1}$ in the past four decades (e.g. Sundquist et al., 1979; Brewer, 1983; Winn et al., 1998; Takahashi et al., 2003; Keeling et al., 2004; Bates et al., 2012). And an increasing rate of the surface ocean carbon pool of $\sim 0.3 \, \text{Pg C yr}^{-1}$

20 has been included in a schematic illustration of the global carbon cycle in 1990s (Houghton, 2007), though without any reasoning. If this value is correct, it accounts for $> 10\%$ of recent oceanic uptake rates of anthropogenic CO_2. Unfortunately, it is invalid to estimate the global R_{equ} using a uniform δ DIC (e.g. Brewer et al., 1997; Li et al., 2001), since sea surface RF varies very much over the global ocean surface

25 (Sabine et al., 2004).

  In this study, we attempt to examine R_{equ} over the global ocean surface, based on the recently compiled distribution datasets of global ocean surface $p\text{CO}_2$ (Takahashi et al., 2009), surface TAlk (Key et al., 2004; Lee et al., 2006), and upper mixed layer depth (MLD) (de Boyer Montégut et al., 2004). Along with the continually measured

atmospheric CO_2 concentrations at the Mauna Loa station (http://www.esrl.noaa.gov/gmd/ccgg/trends/), we also attempt to evaluate the global R_{equ} evolution from 1960s to 2000s, so as to assist future predictions of changes in this meaningful component of oceanic carbon sink.

2 Materials and methods

2.1 Primary data compilation

The monthly sea surface pCO_2, temperature, and salinity have been compiled over grid boxes of 4° (latitude) ×5° (longitude) by Takahashi et al. (2009) for a reference year 2000 (Version October 2009). Corresponding TAlk was reconstructed from the sea surface temperature and salinity in the Takahashi et al. (2009) dataset, using Lee et al. (2006) relationships. Monthly MLD data were obtained from de Boyer Montégut et al. (2004) with horizontal resolution of 2° × 2°. They were reorganized over the Takahashi et al. (2009) grid boxes. At every grid box, the midwinter month of the annual maximum MLD was selected for calculation.

As shown in Fig. 1, totally 1571 grid boxes were synthesized in this study, covering the total area of 304.4×10^6 km^2, accounting for 93.23 % of the open ocean area (326.5×10^6 km^2). The latter value is adopted by Takahashi et al. (2009), which is consistent with the recently-estimated global ocean surface area (361.8×10^6 km^2) by Charette and Smith (2010) minus the surface areas of continental shelves and deep marginal seas (~ 8 %).

Sea surface DIC concentrations and RF values in the midwinter month were calculated from sea surface pCO_2, temperature, salinity, and the corresponding sea surface TAlk, using the calculation program CO2SYS.xls (Pelletier et al., 2011), which is an updated version of the original CO2SYS.EXE (Lewis and Wallace, 1998). The dissociation constants for carbonic acid were those determined by Millero et al. (2006), and the dissociation constant for the HSO_4^- ion was determined as per Dickson (1990).

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As the sea surface pCO$_2$ data have an uncertainty level of ±2.5 µatm (Takahashi et al., 2009), and the global mean uncertainty in TAlk reconstruction is at a level of ±8 µmol kg^{-1} (Lee et al., 2006), the corresponding uncertainty in DIC was estimated to be ±9 µmol kg^{-1} (Lenton et al., 2012). For the data quality assurance purpose, the wintertime distributions of sea surface pCO$_2$ for a reference year 2000, climatological wintertime TAlk and MLD, along with the corresponding months, and the calculated wintertime sea surface DIC and RF for the reference year 2000, were all presented in the Supplement. Generally, the reconstructed sea surface TAlk and thereby calculated sea surface RF maps agreed well with those field-data based results (e.g. Key et al., 2004; Sabine et al., 2004), giving confidence in the data reconstruction based on Lee et al. (2006) relationships and the calculation using the CO2SYS program.

Decadal mean xCO$_2^{air}$ and δxCO$_2^{air}$ data were based on the Mauna Loa station data released by NOAA/ESRL at http://www.esrl.noaa.gov/gmd/ccgg/trends/. We assumed that atmospheric CO$_2$ was globally mixed well on this time scale, and thus the decadal δxCO$_2^{air}$ values above global oceans were the same everywhere.

2.2 Ocean surface chemical buffering capacity assessments

To evaluate the sea surface δDIC in response to the δxCO$_2^{air}$ at every grid box, we rewrote the eloquent definition of RF (Broecker et al., 1979; Sundquist et al., 1979) as δDIC$/\delta x$CO$_2^{air}$ = δDIC$/\delta p$CO$_2\cdot(P - p$H$_2$O$)$ = DIC$/p$CO$_2/$RF$\cdot(P - p$H$_2$O$)$, where P is the atmospheric pressure at sea level, pH$_2$O is saturated water vapor pressure. During calculation, P was replaced by a constant value of 1.007 atm (i.e. approximately 1.020× 10^5 Pa in winter), while pH$_2$O was calculated from SST and salinity using the Weiss and Price (1980) equation. Both DIC and pCO$_2$ were the wintertime ocean surface values, and RF was determined by TAlk and pCO$_2$. Clearly the ratio of δDIC to δxCO$_2^{air}$ was also a measure of the seawater chemical buffering capacity.

According to a quasi-steady-state assumption, both ocean circulation and the alkalinity field may have scarcely been changed in the past few centuries (Thomas et al.,

2001; Caldeira et al., 2007; Bates et al., 2012). To illuminate the atmospheric forcing on the ocean surface carbonate system, we defined "steady-state sea surface pCO_2" in a given decade by scaling Takahashi et al. (2009) data (for a reference year 2000) to the change in xCO_2^{air} from the corresponding time period. Although the "steady-state sea surface pCO_2" is unnecessary to be exactly real, many researchers estimate a mean sea surface pCO_2 growth rate close to the xCO_2^{air} value over the past several decades. See Lenton et al. (2012), Lauvset and Gruber (2014), and references therein. Using the "steady-state sea surface pCO_2", the climatological sea surface TAlk, temperature, and salinity, we calculated out those "steady-state sea surface DIC" concentrations and corresponding RF values at the arithmetically mean xCO_2^{air} levels in the preindustrial era, in 1960s, in 1970s, in 1980s, in 1990s, in 2000s, and in the IPCC IS92a scenario where atmospheric CO_2 increases to 723 ppm by the end of this century. And then the δDIC to δxCO_2^{air} ratio was obtained for every xCO_2^{air} scenario.

2.3   Global R_{equ} estimation

We examined the R_{equ} following two procedures. For the reference year 2000, we calculated the δDIC potential at every grid box based on the above estimated δDIC to δxCO_2^{air} ratio and the decadal mean δxCO_2^{air} datum between mid-1995 and mid-2005. Thus we can obtain an integral estimate of the global R_{equ} from $\sum(\delta\text{DIC}\cdot\text{density}\cdot\text{MLD}\cdot\text{area})/0.9323$, where 0.9323 or 93.23 % is the proportion ratio of the synthesized grid boxes in the total open ocean area (see Sect. 2.1). The climatological wintertime MLD ranged from 16 m in the equatorial zone to 520 m in high-latitude regions (de Boyer Montégut et al., 2004). Although the convective mixing in high latitudes induces deep water to outcrop at the surface, a box model considering this variability (Crane, 1982) yields an insignificant difference from the Oeschger et al. (1975) two-layer diffusion model of the oceans. This is because the preindustrial "natural" fluxes of CO_2 into and out of global oceans, each approximately 70 Pg C yr^{-1}, are nearly balanced, and individually several times the anthropogenic CO_2 fluxes (Denman et al., 2007). In this

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study, if the wintertime MLD was deeper than 100 m at any grid box, we replaced it by 100 m, as this is the approximate MLD to be fully ventilated in a decade. Over the 1571 grid boxes under study, the area weighted effective wintertime MLD was estimated at 78 m.

For the decadal R_{equ} estimation from 1960s to 2000s, the Sundquist and Plummer (1981) procedure was used. Briefly, we directly calculated out the wintertime "steady-state sea surface DIC" pool in every decade from $\sum(\text{DIC}\cdot\text{density}\cdot\text{MLD}\cdot\text{area})/0.9323$, where DIC was calculated using the climatological sea surface TAlk, temperature, salinity, and the above-mentioned "steady-state sea surface pCO_2" in the given decade. Thus the difference of the two wintertime "steady-state sea surface DIC" pools in neighboring decades, i.e. the global R_{equ}, was obtained.

In this study, we only calculated δDIC potential and R_{equ} over decadal periods. This is because the chemical buffering capacity slows down CO_2 re-equilibration across the air–sea interface (Zeebe and Wolf-Gladrow, 2001). In order to fully ventilate the oceanic CO_2 from a mean upper mixed layer, a time span of twice the Craig (1957) mixed layer DIC residence time ($5 \times 2 = 10$ years) is needed.

3 Results and discussion

3.1 Potentials of ocean surface DIC to rise in response to the rising atmospheric CO_2

For the reference year 2000, the potential ratio of air–sea re-equilibration induced ocean surface δDIC (in wintertime) to $\delta x CO_2^{air}$ ranged from 0.284 to 0.700 μmol kg^{-1} ppm^{-1} (Fig. 1a). Very low δDIC : $\delta x CO_2^{air}$ ratios of 0.284 to 0.380 μmol kg^{-1} ppm^{-1} were calculated in the northern North Pacific and in the Southern Oceans, while very high ratios of 0.590 to 0.700 μmol kg^{-1} ppm^{-1} were obtained in the western and central parts of those subtropical oceanic gyres. Figure 2 showed two positive correlations of δDIC : $\delta x CO_2^{air}$ ratio vs. SST and of δDIC : $\delta x CO_2^{air}$ ratio vs.

sea surface TAlk : DIC ratio. Clearly the ocean surface chemical buffering capacity was mainly controlled by carbonate system (Li et al., 2001), rather than another possible controlling factor of SST (Broecker et al., 1979; Sundquist et al., 1979; Sundquist and Plummer, 1981; Zeebe and Wolf-Gladrow, 2001). Nowadays most wintertime surface

5 TAlk : DIC ratios in open oceans ranged from 1.045 in Southern Oceans to 1.180 in low-latitude areas (Fig. 3). In high-latitude regions, sea surface waters absorb a considerable amount of CO$_2$ from the atmosphere due to the high solubility of CO$_2$ at low temperatures, resulting in the low TAlk : DIC ratios. According to Egleston et al. (2010) and Wang et al. (2013), a decrease in the seawater TAlk : DIC ratio to 1 : 1 leads to

10 the decline in chemical buffering capacity, thereby the very low $\delta\,\mathrm{DIC} : \delta x\mathrm{CO}_2^{\mathrm{air}}$ ratios were often observed in cold and high-latitude regions (Fig. 1a). In equatorial upwelling areas in the eastern Pacific, relatively low sea surface $\delta\,\mathrm{DIC} : \delta x\mathrm{CO}_2^{\mathrm{air}}$ ratios of 0.383 to 0.500 µmol kg^{-1} ppm^{-1} were also revealed (Fig. 1a), due to the upwelling of high-pCO$_2$ water from depth.

15 It is worthwhile to note that the air–sea re-equilibration of CO$_2$ over ocean surface is obstructed by the slow gas exchange and/or disturbed by interannual changes in vertical mixing modes (e.g. Gruber et al., 2002). Therefore, the above-estimated $\delta\,\mathrm{DIC} : \delta x\mathrm{CO}_2^{\mathrm{air}}$ ratios may differ from the real. In the decadal time horizon, impacts of the air–sea re-equilibration time (τ) must be considered. Following Zeebe and Wolf-

20 Gladrow (2001), $\tau(\mathrm{CO}_2) = \mathrm{MLD}/k \times (\mathrm{DIC}/[\mathrm{CO}_2^*]/\mathrm{RF})$, where k is the gas transfer velocity, and [CO$_2^*$] is the concentration of free CO$_2$. During calculation, the effective MLD ranged from 16 m to 100 m (see Sect. 2.3), while k was set to the global mean gas transfer velocity value (3.50 m d^{-1}) derived from radiocarbon measurements (Sweeney et al., 2007). According to the estimation results presented in the Supplement, τ (CO$_2$)

25 varied from 85 days in the equatorial zone and high-latitude regions to 677 days in mid-latitude regions, with an globally area-weighted average of 340 days. If we divided the global mean τ (CO$_2$) value of 340 days by 3 months (90 days) every winter, a residence time of DIC in the surface ocean was estimated as 3.8 years, which was similar to the value ($\sim$ 5 years) adopted by earlier box model researchers (e.g. Craig, 1957; Bolin and

Eriksson, 1959). This τ (CO$_2$) value meant that the air–sea disequilibrium of DIC declined, in the time span of 3.8 years, to 37 % ($\sim 1/e$) of its initial value (Zeebe and Wolf-Gladrow, 2001). Therefore, in the time horizon of 10 years, the air–sea re-equilibration induced real δ DIC values were expected to reach $1 - (0.37)^{(10/3.8)} = 93\%$ of the potentials. Even in the worst condition where $\tau(\text{CO}_2) = 677$ days, the air–sea re-equilibration induced real δ DIC values were expected to reach $1 - (0.37)^{(10/(667/90))} = 74\%$ of their potentials.

To assess the real δ DIC over the ocean surface, repeat observations of ocean surface carbonate chemistry may help (e.g. Byrne et al., 2010; Feely et al., 2012). In this study, however, long-term time series results from the two US JGOFS time series study sites located in the North Pacific and North Atlantic subtropical gyres, i.e. the Hawaii Ocean Time series (HOT) and the Bermuda Atlantic Time-series Study (BATS), were used as checking values.

Figure 1a shows that, the two US JGOFS time series study sites had very high δ DIC : δxCO$_2^{\text{air}}$ ratios of 0.596 µmol kg^{-1} ppm^{-1} (HOT) and 0.63 to 0.67 µmol kg^{-1} ppm^{-1} (BATS). Considering the decadal mean δxCO$_2^{\text{air}}$ value of 1.91 ± 0.56 ppm yr^{-1} from mid-1995 to mid-2005 (based on the Mauna Loa station data released by NOAA/ESRL at http://www.esrl.noaa.gov/gmd/ccgg/trends/), the corresponding wintertime δ DIC was expected to be 1.14 µmol kg^{-1} yr^{-1} (HOT) and 1.20 to 1.28 µmol kg^{-1} yr^{-1} (BATS) during this decade. Both were comparable to the field-measured increasing rates of sea surface salinity normalized DIC, i.e. 1.2 ± 0.1 µmol kg^{-1} yr^{-1} at HOT from 1988 to 2002 (Keeling et al., 2004) and 1.08 ± 0.06 µmol kg^{-1} yr^{-1} at BATS from 1983 to 2011 (Bates et al., 2012). At the BATS site, although the wintertime τ (CO$_2$) was estimated to be a very long time span of > 550 days (see the Supplement), the observed mixed layer DIC rise at the site only fell short of the potential δ DIC by 10 % to 15 %. This gave us confidence in our ocean surface chemical buffering capacity assessment and δ DIC estimation, which should be close to the real DIC rise rate on the decadal time scale.

Over the global ocean surface, we worked out an area-weighted average of winter-time ratio of potential $\delta\,\mathrm{DIC}:\delta\,x\mathrm{CO}_2^{\mathrm{air}}$ at $0.536\,\mu\mathrm{mol\,kg^{-1}\,ppm^{-1}}$ for the reference year 2000. Therefore, the global mean wintertime $\delta\,\mathrm{DIC}$ from mid-1995 to mid-2005 was expected to be $1.02\,\mu\mathrm{mol\,kg^{-1}\,yr^{-1}}$, nearly the same as the previously estimated rates in the past four decades (e.g. Sundquist et al., 1979; Brewer, 1983; Winn et al., 1998; Gruber et al., 2002; Takahashi et al., 2003; Keeling et al., 2004; Bates et al., 2012). Note that the decadal mean $\delta x\mathrm{CO}_2^{\mathrm{air}}$ value has increased by 57 % from $1.21 \pm 0.53\,\mathrm{ppm\,yr^{-1}}$ in 1970s to $1.92 \pm 0.37\,\mathrm{ppm\,yr^{-1}}$ in 2000s, based on the Mauna Loa station data released by NOAA/ESRL at http://www.esrl.noaa.gov/gmd/ccgg/trends/. The nearly consistent values of $\delta\,\mathrm{DIC}$ during the past decades showed a significant decline of ocean surface chemical buffering capacity (Fig. 4). As compared with the preindustrial scenario where $x\mathrm{CO}_2^{\mathrm{air}}$ was 280 ppm, the potential sea surface $\delta\,\mathrm{DIC}:\delta x\mathrm{CO}_2^{\mathrm{air}}$ ratio for the reference year 2000 may have decreased by 31 % (Fig. 4). The decline of chemical buffering capacity over the ocean surface is consistent with the general trend of the ocean acidification.

3.2 Ocean surface anthropogenic CO$_2$ accumulation rates

Synthesizing the $\delta\,\mathrm{DIC}:\delta x\mathrm{CO}_2^{\mathrm{air}}$ and the MLD distribution data, under the decadal mean $\delta x\mathrm{CO}_2^{\mathrm{air}}$ forcing from mid-1995 to mid-2005, the global distribution of R_{equ} during the decade were presented in Fig. 1b. High values of 95 to $133\,\mathrm{mmol\,m^{-2}\,yr^{-1}}$ were obtained in mid-latitude areas, where both high $\delta\,\mathrm{DIC}:\delta x\mathrm{CO}_2^{\mathrm{air}}$ ratio and relatively deep MLD occurred. The equatorial zone showed very low R_{equ} values of 15 to $65\,\mathrm{mmol\,m^{-2}\,yr^{-1}}$, as this zone was associated with low to moderate $\delta\,\mathrm{DIC}:\delta x\mathrm{CO}_2^{\mathrm{air}}$ ratios and very shallow MLD. The North Pacific and Southern Oceans had moderate R_{equ} values of 65 to $95\,\mathrm{mmol\,m^{-2}\,yr^{-1}}$, due to the low $\delta\,\mathrm{DIC}:\delta x\mathrm{CO}_2^{\mathrm{air}}$ ratios and deep MLD. As compared with annually net air–sea CO$_2$ fluxes, typically from $-1000\,\mathrm{mmol\,m^{-2}\,yr^{-1}}$

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(CO$_2$ release from seawater) to 2000 mmol m^{-2} yr^{-1} (CO$_2$ uptake by seawater) according to Takahashi et al. (2009), R_{equ} was usually one or two magnitude levels lower.

The globally area-weighted average of R_{equ} during the decade from mid-1995 to mid-2005 was estimated at 80 ± 24 mmol m^{-2} yr^{-1}. Given the surface area of global open ocean of 326.5×10^6 km^2 (Takahashi et al., 2009), the decadal mean value of global R_{equ} from mid-1995 to mid-2005 was recalculated as 0.31 Pg C yr^{-1}, suggesting that R_{equ} accounted for 12.4 to 14.1 % of recent oceanic anthropogenic CO$_2$ uptake rates (as estimated from 2.2 ± 0.4 Pg C yr^{-1} to 2.5 ± 0.5 Pg C yr^{-1} by different authors, see Sect. 1).

During the past five decades, decadal average of xCO$_2^{air}$ rises from 320 ± 3 ppm in 1960s to 331 ± 4 ppm in 1970s, to 345 ± 5 ppm in 1980s, to 360 ± 5 ppm in 1990s, and to 379 ± 7 ppm in 2000s, based on the Mauna Loa station data released by NOAA/ESRL at http://www.esrl.noaa.gov/gmd/ccgg/trends/. Correspondingly, the air–sea re-equilibration associated upper (100 m) ocean pools of DIC potentially increased (data not reported). The associated global open ocean R_{equ} increased from earlier 0.21 Pg C yr^{-1} (between 1960s and 1970s) to later 0.27 Pg C yr^{-1} (between 1970s and 1980s) and 0.26 Pg C yr^{-1} (between 1980s and 1990s) (Fig. 5). Between 1990s and 2000s, the DIC pool increase gave the same ocean surface anthropogenic CO$_2$ accumulation rate of 0.31 Pg C yr^{-1} as the above RF-based R_{equ} value. The global open ocean R_{equ} rise during the past five decades was primarily driven by the increase of δxCO$_2^{air}$ from relatively low rates of 0.8 ± 0.4 ppm yr^{-1} in 1960s to a very high rate of 1.9 ± 0.4 ppm yr^{-1} in 2000s (see Sect. 1). However, the ratio of $R_{equ} : \delta x$CO$_2^{air}$ (i.e. specific R_{equ}) steadily declined from earlier 0.198 Pg C ppm^{-1} (between 1960s and 1970s) to recent 0.167 Pg C ppm^{-1} (between 1990s and 2000s) (Fig. 5). This change suggested again that the chemical buffering capacity in the open ocean surface declined by 16 % during the past 50 years.

In the IPCC IS92a scenario where atmospheric CO_2 increases to 723 ppm by the end of this century, the ocean surface TAlk : DIC ratio inevitably decreased (Fig. 3), leading to a very low area-weighted averaged ratio of $\delta DIC : \delta xCO_2^{air}$ in the global ocean surface (0.217 µmol kg^{-1} ppm^{-1}) (Fig. 4). The exhaustion of chemical buffering capacity over the ocean surface may result in a decline of global open ocean R_{equ} in the second half of this century, if the future δxCO_2^{air} value is no higher than 5 ppm yr^{-1}. This issue has been discussed earlier (e.g. Li et al., 2001; Sabine et al., 2004) and needs more investigations.

To predict future changes in R_{equ}, many natural uncertainties may come from our quasi-steady-state assumption. Nowadays several large-scale circulation and/or biogeochemical changes (e.g. changes in temperature, salinity, and/or dissolved oxygen) have been detected in the ocean. See McNeil1 and Matear (2013) and references therein. According to some modeling results, the strength of oceanic chemical buffering capacity is very dependent on the model ocean state (e.g. Smith and Marotzke, 2008), as it affects all the SST, MLD, pCO_2, and the TAlk field. For example, deep ocean waters comprise excess carbonate-ion due to dissolution of calcium carbonate. These water masses that have upwelled to the surface can effectively buffer anthropogenic CO_2 (Honjo, 1997). However, as a consequence of the future global warming, the thermocline may become a more powerful boundary between ocean surface and deep waters, leading to additional but unfavorable uncertainties on R_{equ}. To lower these uncertainties, a 3-D global ocean carbon model with realistic physics is required (e.g. Doney et al., 2004, 2009b).

4   Concluding remarks

We investigated potentials of ocean surface DIC to rise in response to the rising atmospheric CO_2 and the corresponding anthropogenic CO_2 accumulation rates over the global open ocean surface. The air–sea re-equilibration of upper (100 m) oceans signif-

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icantly contributed to atmospheric CO_2 rise mitigation, accounting for a non-negligible component (likely 12.4 to 14.1 %) of the recent oceanic sink for anthropogenic CO_2. From 1960s to 2000s, owing to the increasing atmospheric CO_2 rise rate, the anthropogenic CO_2 accumulation rate over the global open ocean surface likely increased by 47 %. However, the air–sea re-equilibration induced ocean surface anthropogenic CO_2 accumulation potential under a unit atmospheric CO_2 rise rate declined by 16 % during the same period. By the end of this century, the ocean surface chemical buffering capacity against the atmospheric CO_2 rise may further decline by 78 %, if the possible changes in ocean circulation and the ocean surface TAlk field were ignored.

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Wintertime sea surface potential δDIC : δxCO$_2$^{air} ratio
(μmol kg^{-1} ppm^{-1})

0.68 - 0.71
0.65 - 0.68
0.62 - 0.65
0.59 - 0.62
0.56 - 0.59
0.53 - 0.56
0.50 - 0.53
0.47 - 0.50
0.44 - 0.47
0.41 - 0.44
0.38 - 0.41
0.35 - 0.38
0.32 - 0.35
0.28 - 0.32

R_{equ} (mmol m^{-2} yr^{-1})

125 - 133
115 - 125
105 - 115
95 - 105
85 - 95
75 - 85
65 - 75
55 - 65
45 - 55
35 - 45
25 - 35
15 - 25
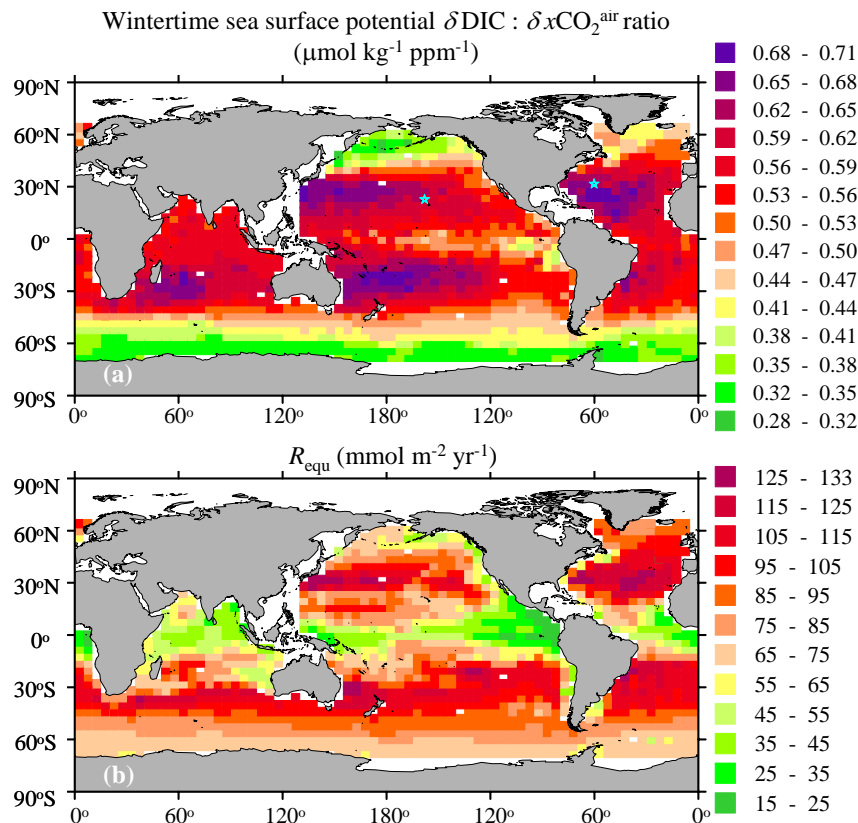
Figure 1. Wintertime distributions of sea surface chemical buffering capacity against the atmospheric CO$_2$ changes for a reference year 2000 **(a)** and the chemical buffering capacity induced ocean surface anthropogenic CO$_2$ uptake rate in the decade from mid-1995 to mid-2005 **(b)**. Stars with the colour of cyan in **(a)** are sites of the Hawaii Ocean Time series program (HOT) and Bermuda Atlantic Time-series Study (BATS).
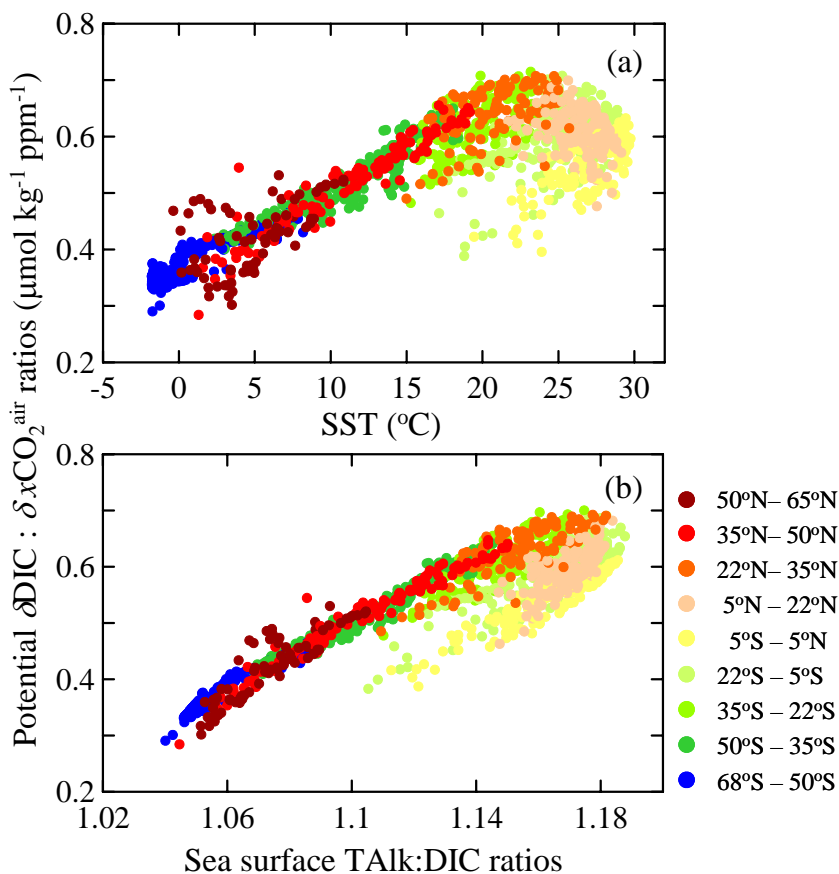
Figure 2. Wintertime surface potential δDIC : δxCO$_2^{air}$ ratio in global open oceans as functions of sea surface temperature **(a)** and of sea surface TAlk : DIC ratio **(b)** for a reference year 2000. Coloured close cycles show different latitude.
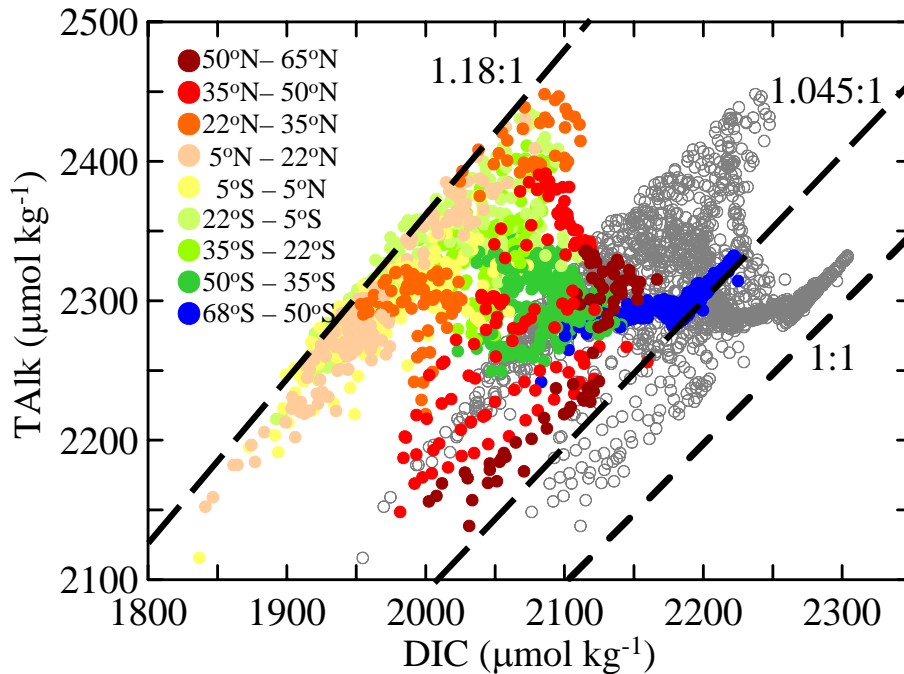
Figure 3. Wintertime surface TAlk vs. DIC in global open oceans. Coloured close cycles show the reference year 2000 data with different latitude, while the grey open circles denote a future scenario with the high atmospheric CO$_2$ level of 723 ppm at the end of this century, according to the IS92a scenario given in Annex II of the IPCC Third Assessment Working Group I report (http://www.ipcc-data.org/observ/ddc_co2.html).
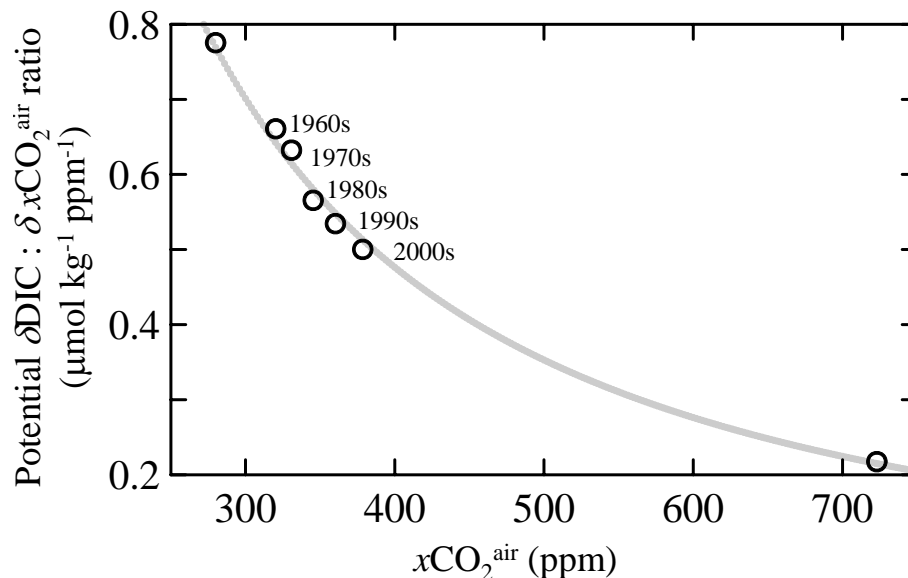
Figure 4. Area-weighted average of the wintertime ocean surface $\delta\,\mathrm{DIC}:\delta x\mathrm{CO}_2^{\mathrm{air}}$ ratio as a function of the $x\mathrm{CO}_2^{\mathrm{air}}$ level, where the low $x\mathrm{CO}_2^{\mathrm{air}}$ of 280 ppm and the high $x\mathrm{CO}_2^{\mathrm{air}}$ of 723 ppm denote the preindustrial scenario and the future scenario at the end of this century, respectively, and the other $x\mathrm{CO}_2^{\mathrm{air}}$ levels correspond to those decadal average values from 1960s to 2000s. The grey curve shows the best fitted exponential curve, $\delta\,\mathrm{DIC}/\delta x\mathrm{CO}_2^{\mathrm{air}} = 1495.6 \times (x\mathrm{CO}_2^{\mathrm{air}}/\mathrm{ppm})^{-1.3439}$.
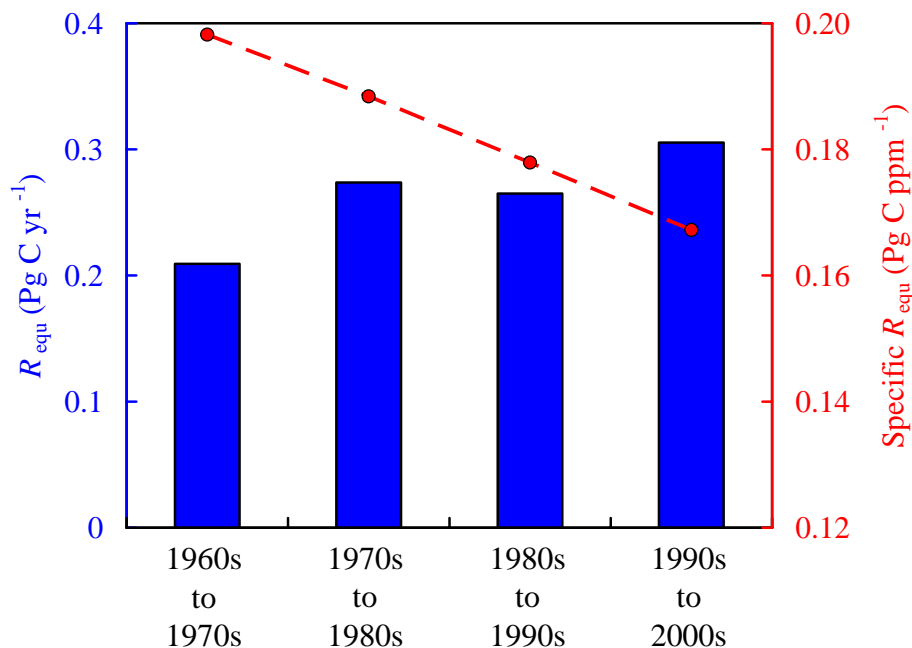
Figure 5. Evolution of the chemical buffering capacity induced anthropogenic CO_2 uptake rate over ocean surface from 1960s to 2000s (columns) and the specific rate at the unit change in atmospheric CO_2 concentration (dots and the dashed line).

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