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The non-steady state oceanic CO_2 signal: its importance, magnitude and a novel way to detect it

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Abstract. The role of the ocean has been pivotal in modulating rising atmospheric CO_2 levels since the industrial revolution, sequestering nearly half of all fossil-fuel derived CO_2 emissions. Net oceanic uptake of CO_2 has roughly doubled between the 1960s ($\sim 1\,Pg\,C\,yr^{-1}$) and 2000s ($\sim 2\,Pg\,C\,yr^{-1}$), with expectations that it will continue to absorb even more CO_2 with rising future atmospheric CO_2 levels. However, recent CO_2 observational analyses along with numerous model predictions suggest the rate of oceanic CO_2 uptake is already slowing, largely as a result of a natural decadal-scale outgassing signal. This recent CO_2 outgassing signal represents a significant shift in our understanding of the oceans role in modulating atmospheric CO_2. Current tracer-based estimates for the ocean storage of anthropogenic CO_2 assume the ocean circulation and biology is in steady state, thereby missing the new and potentially important "non-steady state" CO_2 outgassing signal. By combining data-based techniques that assume the ocean is in a steady state, with techniques that constrain the net oceanic CO_2 uptake signal, we show how to extract the non-steady state CO_2 signal from observations. Over the entire industrial era, the non-steady state CO_2 outgassing signal ($\sim 13 \pm 10\,Pg\,C$) is estimated to represent about 9 % of the total net CO_2 inventory change ($\sim 142\,Pg\,C$). However, between 1989 and 2007, the non-steady state CO_2 outgassing signal ($\sim 6.3\,Pg\,C$) has likely increased to be ~ 18 % of net oceanic CO_2 storage over that period ($\sim 36\,Pg\,C$). The present uncertainty of our data-based techniques for oceanic CO_2 uptake limit our capacity to quantify the non-steady state CO_2 signal, however with more data and better certainty estimates across a range of diverse methods, this important and growing CO_2 signal could be better constrained in the future.

1 Introduction

1.1 The evolution of our understanding of the oceanic CO_2 sink

1.1.1 Our traditional steady state view of the oceanic CO_2 cycle

For thousands of years before the onset of the industrial revolution (~ 1800 AD), carbon cycling between atmospheric, land and oceanic biospheres was in relative steady state. Although large gross exchanges of CO_2 were occurring annually between land, atmosphere and oceans, atmospheric CO_2 remained relatively constant at about 280 ± 5 µatm, implying a steady state carbon cycle (Etheridge et al., 1998). Humans, via the burning of fossil fuel carbon, have emitted about 530 Pg C into the atmosphere, perturbing atmospheric CO_2.

Quantifying the flows, exchanges and storage of this anthropogenic CO_2 in the earth system has been a primary objective for the biogeochemical research community. Due to the heterogeneity in both space and time within the land carbon system, partitioning the global carbon storage between land and ocean has largely relied on our more certain understanding of the oceans storage of anthropogenic CO_2. Fortunately, a number of different independent methods have allowed researchers to quantify the oceanic anthropogenic CO_2 sink (Quay et al., 1992; Gruber et al., 1996; Keeling et al., 1996; Gruber and Keeling, 2001; McNeil et al., 2003; Sabine et al., 2004; Waugh et al., 2006; Khatiwala et al., 2009). Fundamental to these estimates is the assumption that large-scale natural cycling of carbon through biological and

circulation pathways have remained in steady state throughout the 20th century, with the anthropogenic perturbation acting passively on top of that large natural but unchanging "background" carbon cycle. This steady state assumption was valid during most of the 20th century whereby any climate-related alterations to the oceanic anthropogenic CO_2 sink have been small in comparison to the large emissions signal itself (Sarmiento et al., 1998; Matear and Hirst, 1999). Although the steady state assumption may have been adequate for the 20th century due to the small impact on net oceanic CO_2 uptake, as discussed below, this is no longer the case for the 2st century.

1.1.2 The emerging non-steady state oceanic CO_2 signal

Over recent decades, oceanographers have observed large-scale decadal and longer timescale trends in the ocean associated with biological changes, circulation changes and temperature-related solubility changes. The first observational research documenting large-scale decadal changes in the oceans circulation pathways were shown in the 1990s with temperature and salinity alterations in major ventilation pathways of the ocean (Wong et al., 1999). Since then the number of hydrographic measurements have increased, leading to a detailed understanding of the large-scale ocean warming trend (Levitus et al., 2000) as well as salinity changes associated with the amplification of the hydrological cycle (Durack and Wijffels, 2010; Helm et al., 2010). In the case of biogeochemistry, although nutrients were hypothesized to be changing (Pahlow and Riebesell, 2000), it was a suite of studies showing declining and/or changing oxygen concentrations in various parts of the ocean (Emerson et al., 2001; Matear et al., 2000; Whitney et al., 2007; Stendardo and Gruber, 2012), which confirmed that large-scale circulation and/or biological changes were impacting biogeochemical cycles.

A new suite of climate models (Wetzel et al., 2005; Le Quéré et al., 2007; Lovenduski et al., 2007; Matear and Lenton, 2008; Rodgers et al., 2008) driven with observed wind, heat and freshwater fluxes showed that beginning in the late 1980s, net CO_2 uptake started to level off. Oceanic CO_2 uptake was not increasing in the way it should be if the uptake was only a function of increasing atmospheric CO_2 levels and was quite aptly described by Sarmiento et al. (2010) as "somewhat of a surprise".

Le Quéré et al. (2007) combined this modeling result with atmospheric CO_2 measurements over the Southern Ocean to postulate that the net oceanic CO_2 sink was leveling in response to an observed intensification of winds over the Southern Ocean that caused higher outgassing of naturally CO_2-rich deep waters, partially offsetting a large anthropogenic CO_2 uptake signal. Le Quéré et al. (2007) and a follow-up model study by Lovenduski et al. (2008) showed that the CO_2 outgassing in the Southern Ocean to be up to 35 % of the anthropogenic CO_2 flux.

These non-steady state ocean carbon changes create systematic biases in many tracer-based techniques that attempt to quantify the anthropogenic CO_2 storage in the ocean and these biases will continue to grow as the non-steady state ocean evolves through the 21st century. This new development is critically important from an atmospheric CO_2 perspective, since non-steady state changes in the ocean (at least the present outgassing) are a positive CO_2 feedback on atmospheric CO_2 levels. Recent evidence appears to show that the airborne fraction of CO_2 (the fraction of anthropogenic emissions which remain in the atmosphere) maybe increasing (Raupach et al., 2007; Le Quéré et al., 2009; Gloor et al., 2010; Knorr, 2012), and climate-driven oceanic CO_2 outgassing may be playing a role in those atmospheric CO_2 trends. The non-steady state CO_2 signal is what we seek to detect, since without it, the ability to monitor and predict future atmospheric CO_2 levels will be impeded.

In this manuscript we seek to do two things. First, we present a decomposition of total oceanic CO_2 changes over time into natural and anthropogenic, steady and non-steady state components. By doing this we seek to show the important difference between what often is referred to as anthropogenic CO_2 change in the ocean and the very different total net change in CO_2 in the ocean, since they are sometimes incorrectly used interchangeably. But foremost, this decomposition clarifies the differing steady and non-steady components in the oceanic CO_2 signal for budgetary purposes. Second, we investigate and present a simple data-based method to partition the time-evolving CO_2 sink into a steady state and non-steady state signal.

2 Decomposing the time evolution of CO_2 in the Ocean

The net oceanic dissolved inorganic carbon change (ΔDIC_{Net}) between a period of time ($t1$ to $t2$) reflects changes in both natural and anthropogenic carbon dynamics:

$$[\Delta DIC_{Net}] = [\Delta DIC_{Nat}] + [\Delta ACO_2]. \quad (1)$$

Natural changes in DIC (ΔDIC_{Nat}) occur through temperature, biological and ocean circulation changes via climate/ocean variability and change. On top of these natural DIC changes are also changes in DIC due to the oceanic uptake of anthropogenic CO_2 (ΔACO_2).

If there were no net changes to the natural DIC concentrations in the ocean over a given time period (i.e. steady state), then the time-evolving net change would be simply equal to the anthropogenic CO_2 uptake by the ocean (i.e. $\Delta DIC_{Net} = \Delta ACO_2$).

In this steady state world, anthropogenic CO_2 can be treated as a passive solubility tracer such as chlorofluorocarbons (CFCs), whereby its uptake is driven solely by the

atmosphere–ocean gradient, gas exchange and mixing without the need to account for biology or circulation changes. This definition of anthropogenic CO_2 makes tracer-based approaches very attractive. However, as models have shown (Joos et al., 1999; Friedlingstein et al., 2006; Matear and Hirst, 1999; Sarmiento et al., 1998) and observed CO_2 trends show (Le Quéré et al., 2007; Lenton et al., 2012), the ocean CO_2 system is not in steady state, consistent with physical oceanic properties (temperature, salinity, oxygen) that have showed temporal change.

To account for this time-evolving behavior in CO_2 it is therefore necessary to decompose the time evolution of anthropogenic CO_2 (ACO_2) into its steady and non-steady state components as follows:

$$[\Delta ACO_2] = \underbrace{\overline{[\Delta ACO_2]}}_{\text{Steady State}} + \underbrace{[\Delta ACO_2^{'}]}_{\text{Non-Steady State}} \quad (2)$$

where $\overline{\Delta ACO_2}$ is the traditional steady state definition of anthropogenic CO_2 used in the literature, whereby circulation and biological carbon changes remain constant with rising CO_2 in the atmosphere. $\Delta ACO_2^{'}$ is the non-steady state term identified by climate change models whereby anthropogenic CO_2 is modified by changes in circulation and/or biology from global warming (like stratification or warming's effect on CO_2 solubility). This non-steady state term has been explored in ocean biogeochemical models and shows a relatively small but growing non-steady state anthropogenic CO_2 uptake signal by the end of this century (10–20 %) (Sarmiento et al., 1998; Matear and Hirst, 1999; Plattner et al., 2001; Friedlingstein et al., 2006; Matear and Lenton, 2008).

Natural decadal variability and change alter ocean circulation and biology, therefore impacting the time-evolving DIC signal, requiring a separate set of equations:

$$[\Delta DIC_{Nat}] = \underbrace{\overline{[\Delta DIC_{Nat}]}}_{\text{Steady State}} + \underbrace{[\Delta DIC_{Nat}^{'}]}_{\text{Non-Steady State}} \quad . \quad (3)$$

By definition, globally $\overline{\Delta DIC_{Nat}}$ over time is 0, therefore the total changes in the natural carbon cycle (ΔDIC_{Nat}) are equal to the non-steady state changes to the natural carbon cycle ($\Delta DIC_{Nat}^{'}$). For example, $\Delta DIC_{Nat}^{'}$ could be those carbon changes resulting from natural variability in the climate system, such as perhaps those driven from decadal-scale intensification of Southern Ocean winds, El Niño–Southern Oscillation events, trends in remineralization stoichiometry or even regional time-evolving movements in circulation pathways over two different periods of time.

What is important to remember here is that correcting for the natural DIC signal in the ocean from back-calculation techniques, such as ΔC^*, does not account for either the natural non-steady state signal ($\Delta DIC_{Nat}^{'}$) or the anthropogenic non-steady state signal ($\Delta ACO_2^{'}$).

In summary, the time-evolving net DIC signal is the sum of three terms:

$$[\Delta DIC_{Net}] = \underbrace{\overline{[\Delta ACO_2]}}_{\text{Steady State}} + \underbrace{\underbrace{[\Delta ACO_2^{'}]}_{\text{Non-Steady State}} + \underbrace{[\Delta DIC_{Nat}^{'}]}_{\text{Non-Steady State}}}_{\text{Combined Non-Steady State Signal}} \quad . \quad (4)$$

To simplify Eq. (4), we combine them into steady and non-steady state signals:

1. $\overline{\Delta ACO_2}$; the steady state change in ocean CO_2 over time due to rising atmospheric CO_2 in a unchanging ocean.
2. ($\Delta ACO_2^{'} + \Delta DIC_{Nat}^{'}$); the combined non-steady state signal that incorporates how a changing ocean alters DIC in the ocean.

The most important term in Eq. (4) for atmospheric CO_2 modulation is the combined net CO_2 sink (ΔDIC_{Net}); therefore, it is important to investigate and constrain the non-steady state CO_2 signal.

2.1 The anthropogenic non-steady state signal

When introducing the ΔC^* method, Gruber et al. (1996) were clear that their technique required a steady state assumption. The global application of the ΔC^* method was performed by Sabine et al. (2004) and it is important to understand that they estimated the steady state oceanic anthropogenic CO_2 inventory (i.e. $\overline{\Delta ACO_2}$ in Eq. 4) and assumed it was equivalent to the total net change in oceanic CO_2 (i.e. ΔDIC_{Net}). Between 1880 and 1994, Sabine et al. (2004) estimated an anthropogenic CO_2 storage in the ocean of 118 ± 19 Pg C, which was recently increased to ~ 155 Pg C by 2010 based on a different steady state tracer technique (Khatiwala et al., 2009).

In a commentary to *Science*, Ralph Keeling highlighted the important but missing non-steady state anthropogenic signal (i.e. $\Delta ACO_2^{'}$) within the Sabine et al estimate (Keeling, 2005). He noted that "Anthropogenic CO_2" as it has been used traditionally is "an incomplete measure of the change in the ocean carbon content". He further discussed the necessary steady state assumption that oceanic tracer-based techniques require and made a first attempt to calculate the non-steady state anthropogenic CO_2 change in association with recent climate change (i.e. $\Delta ACO_2^{'}$).

Using a box-diffusion model, Keeling (2005) estimated a 13 Pg C outgassing of CO_2 due to the thermodynamic effect of increasing CO_2 in warmer oceanic surface waters up until 1994. With recent climate change until that point, upper ocean density stratification would also have already occurred. Although this stratification likely limits the subduction of water masses into the interior, Keeling (2005) postulated a stable upper ocean would also result in a more efficient (at least initially) biological drawdown of CO_2 from

the surface to the interior. Based on a suite of ocean model simulations, he estimated a net carbon drawdown of +6 Pg C up until 1994. Different non-steady state anthropogenic processes (ocean warming and stratification/biological export) partially offset each other, resulting in a final combined estimate of 7 ± 10 Pg C for $\Delta ACO_2^{'}$ from Keeling (2005).

This non-steady state term for oceanic anthropogenic CO_2 is still less than 10 % of the final anthropogenic CO_2 inventory estimate and well within the total uncertainty of the technique (± 19 Pg C), as noted by Sabine and Gruber (2005). So although $\Delta ACO_2^{'}$ has been known to bias the data-based estimates of anthropogenic CO_2 storage in the ocean, the bias is relatively small (~ 10 %).

However, the most important term, at least over the past twenty years, in Eq. (4) is not $\Delta ACO_2^{'}$ but $\Delta DIC_{Nat}^{'}$ as recent discoveries have shown us.

2.2 The natural non-steady state signal

Le Quéré et al. (2007) showed that wind-speed intensification in the Southern Ocean was not only causing a large natural outgassing of CO_2 as other models showed (Lovenduski et al., 2007; Lenton et al., 2009), but this trend was detected from atmospheric CO_2 observations, although the atmospheric trend is still the subject of debate (Law et al., 2008). Arguably this Southern Ocean outgassing could be the fingerprint of climate change itself, but it could also be simply a natural decadal response and therefore would be mostly identified as a natural non-steady state signal ($\Delta DIC_{Nat}^{'}$). In any case, partitioning this signal into $\Delta ACO_2^{'}$, or $\Delta DIC_{Nat}^{'}$ is not important, since we combine both the natural and anthropogenic non-steady state signals for simplicity.

It is important to emphasize that the above decomposition is relevant for global changes in ocean carbon inventories that can then translated into global air–sea CO_2 fluxes. On a regional basis however, translating carbon inventory changes to regional air–sea CO_2 fluxes could be largely independent. For example a lateral change in the position of a gyre would translate into large changes in $\Delta DIC_{Nat}^{'}$ within the ocean interior without a corresponding air–sea CO_2 flux signature.

Although research has progressed in understanding the regional natural non-steady state CO_2 signal (Le Quéré et al., 2007; Lovenduski et al., 2007; Levine et al., 2008; Goodkin et al., 2011), how important is it on a global scale?

3 Can we detect the global non-steady state CO_2 signal?

Sarmiento et al. (2010) synthesize a suite of different models from earlier studies (Wetzel et al., 2005; Mikaloff-Fletcher et al., 2006; Le Quéré et al., 2007; Lovenduski et al., 2008; Rodgers et al., 2008) to estimate the global magnitude of the combined non-steady state oceanic CO_2 signal between 1989 and 2007. For completeness, here we add the CSIRO biogeochemistry model (Matear and Lenton, 2008) to that suite of model results.

To illustrate the divergence of the time-evolving net oceanic CO_2 uptake in recent decades, we combine the five different model predictions that use time-evolving NCEP atmospheric forcings and compare it to the expected steady state uptake just from atmospheric CO_2 increases alone (Fig. 1).

On average, as reported by Sarmiento et al. (2010), time-varying ocean models take up 0.35 Pg C yr^{-1} less CO_2 between 1989 and 2007 than they would have if ocean circulation and biogeochemistry had remained in steady state. This would equate to a combined non-steady state CO_2 inventory reduction of about 6.3 Pg C between 1989 and 2007 in comparison to the total net CO_2 inventory (ΔDIC_{Net}) of about 36 Pg C from these models (Fig. 1). Each model differs in magnitude, but on average the magnitude of the combined non-steady state CO_2 signal between 1989 and 2007 is about 18 % of the total carbon stored in the ocean over this time period.

By combining the Keeling (2005) and Sarmiento et al. (2010) estimate, the total non-steady state CO_2 outgassing since the industrial revolution would be about 13 ± 10 Pg C, which is about ~ 10 % of the steady state anthropogenic CO_2 inventory (~ 155 Pg C). It is important to emphasize that the Keeling (2005) estimate was made using the Sabine et al. (2004) estimate for anthropogenic CO_2 sink up until 1994. The Sarmiento et al. (2010) model results were made from 1990 onwards, so that by combining these estimates results in a four year overlap. However, if we take the models from Sarmiento et al. (2010) as a gauge, the largest signal in the non-steady state comes after the mid-1990s, so this overlap would probably result in a small bias (~ 0.5 Pg C of the estimate).

Despite the relatively small estimated non-steady state CO_2 signal over the entire industrial era, this non-steady state signal has grown to be about 18 % of net oceanic CO_2 storage between 1989–2007. Given the large magnitude of the non-steady state CO_2 signal simulated in the models since 1989, can we use data-based methods to constrain it?

3.1 The multi-method approach to estimate the non-steady state signal

In recent years there has been a proliferation of new tracer-based techniques to quantify decadal changes in oceanic CO_2 uptake (Hall et al., 2002, 2004; Gloor et al., 2003; Waugh et al., 2006; Khatiwala et al., 2009) that follow on from the C* method (Gruber et al., 1996) and earlier attempts (Chen, 1982). Other techniques using atmospheric observations, i.e. CO_2 inversions or atmospheric O_2/N_2 methods (Ciais et al., 1995; Keeling et al., 1996; Bousquet et al., 2000; Keeling and Garcia, 2002; Patra et al., 2005; Manning and Keeling, 2006) or a combination (Jacobson et al., 2007) are typically lumped together with those ocean-tracer

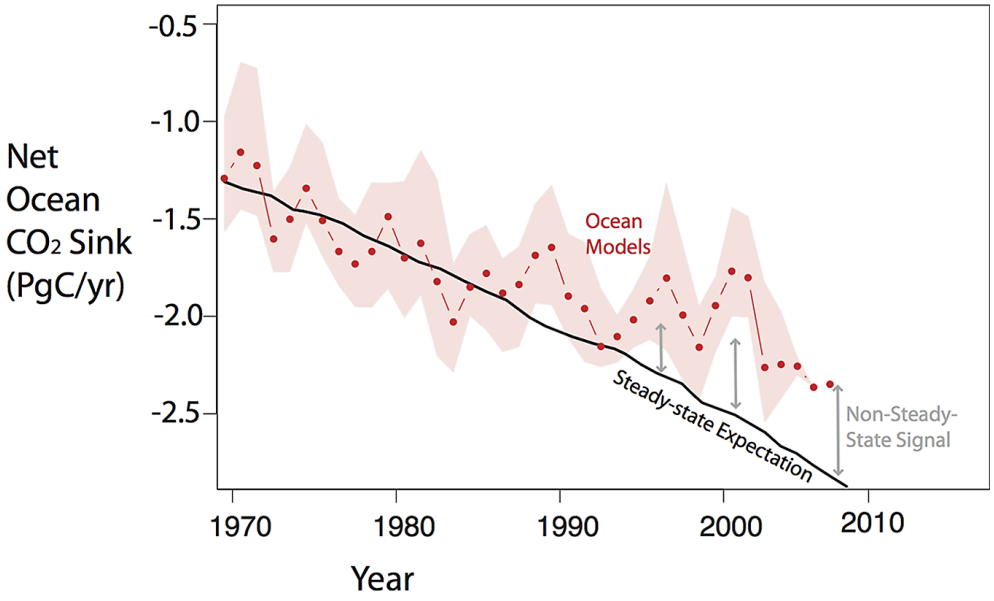

Fig. 1. Illustration of the time-evolving net CO_2 uptake from the ocean since 1970 comparing the expected steady state uptake that assumes constant circulation and biology (black line) with the mean net uptake from five different ocean models that include time-evolving natural forcings (Wetzel et al., 2005; Le Quéré et al., 2007; Lovenduski et al., 2007; Matear and Lenton, 2008; Rodgers et al., 2008). We include the results from the hindcast CSIRO climate model from Matear and Lenton (2008) and the suite of model projections documented in Sarmiento et al. (2010). The expected steady state CO_2 uptake is taken from Mikaloff-Fletcher et al. (2006) as documented by Sarmiento et al. (2010), normalized to the decade of 1970–1980. The average net CO_2 uptake (red dots) was taken as a combined mean between the five different models with minimum and maximum bounds shaded in light red. This is an illustrative figure used to demonstrate the time-evolving changes in the various CO_2 signals within the ocean as described in Eq. 4. The integrated dotted red curve is the total net CO_2 uptake by the ocean (ΔDIC_{Net}), which is about 36 Pg C between 1989 and 2007. The black curve is the expected steady state CO_2 uptake or what has been historically called anthropogenic CO_2 uptake ($\overline{\Delta ACO_2}$), which is about 42 Pg C between 1989 and 2007. The difference between these curves is therefore the combined non-steady state CO_2 loss to the atmosphere ($\Delta ACO_2^{'} + \Delta DIC_{Nat}^{'}$), which comes to about 6.3 Pg C outgassing to the atmosphere between 1989 and 2007 (see Table 2 of Sarmiento et al., 2010).

methods with the assumption they are quantifying the same time-evolving oceanic CO_2 signal, which is not true.

Different data-based techniques constrain different oceanic CO_2 signals. Or to put it another way, each data-based technique has a different sensitivity towards capturing the non-steady state signal in the ocean. For example, the C^* method uses actual carbon measurements, that to some degree will contain some but not all of the non-steady state signal. The multi-method approach here requires the use of methods that capture either the steady-state-state signal or the net oceanic CO_2 signals with the most certainty. A technique which partially captures both the steady state and non-steady state signals is not a method that is helpful when applying the multi-method approach here. To clarify what signal differing data-based techniques are actually constraining, we list them in Table 1.

Most of the ocean-based tracer techniques quantify the steady state anthropogenic CO_2 signal alone ($\overline{\Delta ACO_2}$), while the atmospheric techniques quantify the total time-evolving net CO_2 oceanic signal (ΔDIC_{Net}). Although each method has inherent uncertainties and biases, there is powerful information in treating them as independent, whereby there difference theoretically should constrain the combined non-steady state response.

For an ocean that is changing with climate change and decadal variability, combining steady state methods with total net methods could provide a powerful way to quantify how the oceanic CO_2 sink is actually evolving. For example, the total net CO_2 sink (i.e. ΔDIC_{Net} in Eq. 4) is best captured from two different techniques: the O_2/N_2 atmospheric technique and surface ocean pCO_2 climatologies. On the other hand, CFC-based and ocean inversion methods are the most accurate techniques to capture the steady state anthropogenic CO_2 inventory between two different periods of time. In theory, by comparing the results of these different techniques should produce a testable signal equivalent to the non-steady state oceanic CO_2 change.

The expected steady state anthropogenic CO_2 uptake in the 1990s from oceanic inversions and CFCs is 2–2.2 Pg C yr^{-1} (see Table 2). The total net CO_2 uptake for the 1990s from oceanic pCO_2 climatology and atmospheric O_2/N_2 methods is 1.7–1.9 Pg C yr^{-1}. Solving equation 4 implies that the difference between these constraints is the non-steady state CO_2 signal, implying an outgassing of 0.1 to

Table 1. Data-based techniques to quantify "anthropogenic" CO_2 storage in the ocean.

	Component Constrained in Eq. (4)
Ocean Data-based Techniques	
Ocean DIC MLR on repeat cruises (Slansky et al., 1997; McNeil et al., 2001; Matear and McNeil, 2003; Bates et al., 2006)	? (Not easily identified)
Direct DIC difference from repeat cruises	ΔDIC_{Net}
CFCs, TTDs, C* (Gruber et al., 1996; McNeil et al., 2003; Waugh et al., 2006; Khatiwala et al., 2009)	$\overline{\Delta ACO_2}$
Ocean-based CO_2 Inversions (Gloor et al., 2003; Mikaloff-Fletcher et al., 2007; Gruber et al., 2009)	$\overline{\Delta ACO_2}$
Oceanic ΔpCO_2 climatology (Takahashi et al., 2002)	ΔDIC_{Net}
Atmospheric Data-Based Techniques	
CO_2 Inversions (Ciais et al., 1995; Francey et al., 1995; Bousquet et al., 2000; Patra et al., 2005; Le Quéré et al., 2007)	ΔDIC_{Net}
O_2/N_2 Measurements (Keeling et al., 1996; Battle et al., 2000; Keeling and Garcia, 2002; Bender et al., 2005; Manning and Keeling, 2006)	ΔDIC_{Net}

$0.5\,Pg\,C\,yr^{-1}$ (Table 2). If we assume uncertainties are independent between the different methods (Table 2) within a range of ± 0.4–$0.6\,Pg\,C\,yr^{-1}$, a simple propagation of the uncertainties within a combination of any two of these methods implies a total uncertainty on the multi-method approach of about ± 0.6–$0.8\,Pg\,C\,yr^{-1}$. This uncertainty at present makes the non-steady state signal as estimated through the multi-method approach statistically insignificant given a signal of 0.1 to $0.5\,Pg\,C\,yr^{-1}$ (Table 2).

The application of the multi-method approach, however, illustrates the potential benefit of using such an approach but also challenges us to obtain better observations to reduce these uncertainties amongst the suite of different oceanic CO_2 uptake data-based techniques. It is interesting, however, that models are suggesting a non-steady state CO_2 outgassing ($\sim +0.4\,Pg\,C\,yr^{-1}$) which is nearing the uncertainty limits for a multi-method approach (i.e. ± 0.6–$0.8\,Pg\,C\,yr^{-1}$), implying that into the future, with greater certainty, such a non-steady state CO_2 signal could become observationally statistically significant.

We formulate a revised oceanic carbon budget for the 1989–2007 period (Fig. 2) that takes into account the $\sim +0.4\,Pg\,C\,yr^{-1}$ non-steady state CO_2 outgassing predicted by both the models and somewhat tentatively by the multi-methodological constraint illustrated here.

4 Challenges to reducing uncertainty

The key limitation to this multi-methodological approach today is the current large uncertainty of the different data-based techniques to quantify anthropogenic CO_2 uptake in the ocean. It is not necessarily important which combination of technique is used, but rather we have certainty over its assumptions and application.

Many of the techniques suffer from a lack of measurements, which can be rectified in the future. For example, the pCO_2 database, although good coverage exists in the Northern Hemisphere, complex regimes like the equatorial Pacific and Southern Oceans have large gaps in coverage. However, with autonomous CO_2 measurements increasing, this will change.

One complication with pCO_2 climatologies is associated with the natural outgassing of carbon that enters the ocean via rivers and estuaries. This is an uncertain but necessary constraint for the oceanic carbon budget when using pCO_2 climatologies or oceanic inversions (Jacobson et al., 2007; Gruber et al., 2009). From an atmospheric perspective, this riverine CO_2 outgassing is a steady state signal since the coinciding uptake of CO_2 occurs on land through biomass production. However, from the "raw" pCO_2 climatologies, the riverine CO_2 outgassing needs to be added to the final global ocean estimate. This riverine CO_2 outgassing is estimated to be $+0.45\,Pg\,C\,yr^{-1}$ (Jacobson et al., 2007) with a 50 % uncertainty. The magnitude of this riverine CO_2 outgassing would dampen this techniques ability to detect the non-steady state CO_2 signal, unless that is constrained to a much higher accuracy.

Other techniques like the modern application of CFC-tracers (Waugh et al., 2006; Khatiwala et al., 2009) are not as data-limited and provide the most accurate way of constraining the steady state anthropogenic CO_2 signal over decadal timescales. With temporal CFC or tracer measurements, this

Table 2. Different estimates for the time-evolving oceanic CO_2 uptake between 1990–1999 assuming no uncertainty.

Data-based Technique	Steady State Anthropogenic CO_2 Uptake ($\overline{\Delta ACO_2}$)	Total Net CO_2 Uptake (ΔDIC_{Net})	Non-steady state CO_2 uptake (i.e. $\Delta DIC_{Net} - \overline{\Delta ACO_2}$)
Ocean Inversion (Gruber et al., 2009)	$-2.2\,Pg\,C\,yr^{-1}$		
CFCs (McNeil et al., 2003; Khatiwala et al., 2009)	$-2.0\,Pg\,C\,yr^{-1}$		
Oceanic pCO_2 Climatology		$-1.9\,Pg\,C\,yr^{-1}$	
Atmospheric O_2/N_2 (Keeling and Garcia, 2002; Manning and Keeling, 2006; Bender et al., 2006)		-1.7 to $1.9\,Pg\,C\,yr^{-1}$	
Multi-technique Difference as diagnosed here			$+0.1$ to $+0.5\,Pg\,C\,yr^{-1}$
Suite of Global Climate Models with Recent Climate Variability (Sarmiento et al., 2010)	$-1.97\,Pg\,C\,yr^{-1}$	$-1.46\,Pg\,C\,yr^{-1}$	$+0.35\,Pg\,C\,yr^{-1}$

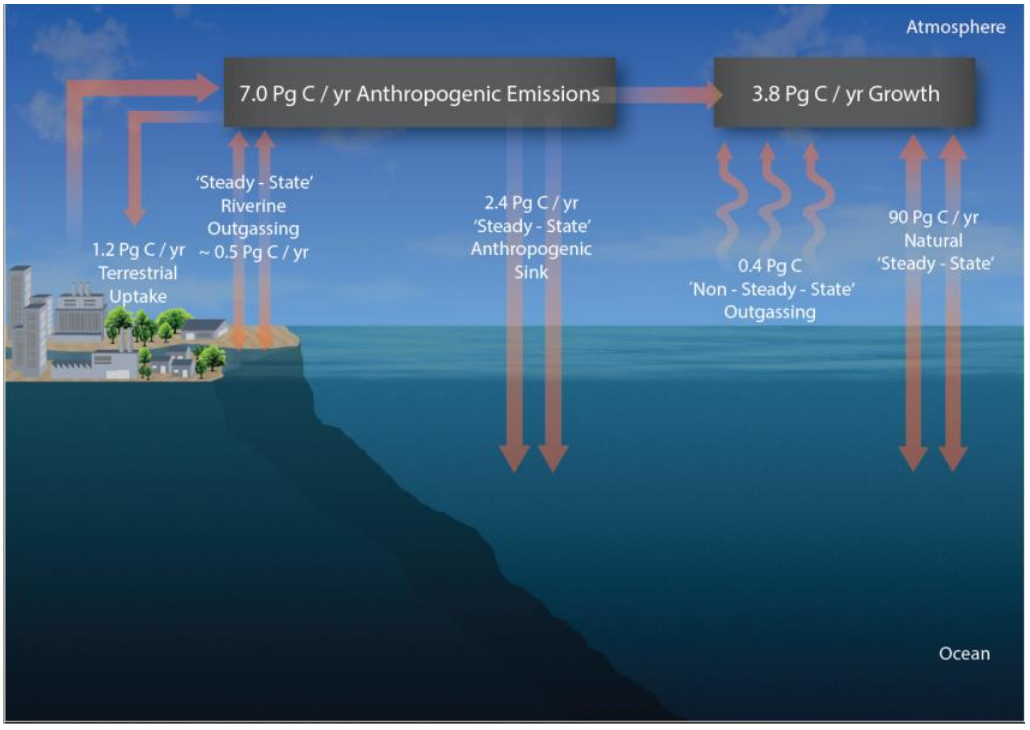

Fig. 2. Estimated non-steady state global carbon budget for 1989–2007 combining oceanic steady state observational estimates with the oceanic non-steady state signal as diagnosed from data and models in this study.

technique could go one-step further to constrain the non-steady state circulation based changes to anthropogenic CO_2, although any changes to the biological pump or natural carbon would be missed.

5 Conclusions

Here we decompose the time evolution of net CO_2 changes in the ocean to clarify the notion of "anthropogenic" CO_2 uptake. Traditionally, oceanic tracer-based techniques have constrained net oceanic storage of CO_2 associated with elevated CO_2 concentrations in the atmosphere under the assumption of a steady state ocean carbon cycle. Both climate-change and decadal changes to the oceanic CO_2 cycle shown recently have clearly marked a new era of non-steady state conditions for CO_2 that was already known from other biogeochemical parameters like oxygen. This global non-steady state CO_2 signal is estimated to have outgassed about $6.3\,Pg\,C$ of CO_2 (or ~ 3 ppm to the atmosphere) between 1989 and 2007, which is $\sim 18\,\%$ of the net oceanic CO_2 uptake rate estimated from models.

After illustrating the different components of the time-evolving oceanic CO_2 sink, we present a simple concept to estimate the non-steady state oceanic CO_2 signal and determine the net change in carbon stored in the ocean. With a

multi-methodological budget approach, we estimate a 0.1–0.5 Pg C yr^{-1} outgassing over the last two decades, however, the uncertainty across the suite of different data-based techniques is too large at present ($\sim$ 0.4–0.6 Pg C yr^{-1}) to provide a significant non-zero estimate of the non-steady state signal.

Although the non-steady state CO_2 signal currently provides a positive feedback to atmospheric CO_2 levels, the future direction and magnitude of the signal is not clear, since some models suggest that recent Southern Ocean outgassing will eventually reverse in the future and absorb greater CO_2 than expected from steady state conditions (Zickfeld et al., 2008).

In the end, atmospheric CO_2 levels only change via the total time-evolving CO_2 changes in the ocean, which based on recent evidence is now entering a new non-steady state mode. Given this emerging mode, the challenge for the observational community is to reduce the uncertainty across a suite of independent data-based techniques to enable the clear separation between the net storage of CO_2 in the ocean and the steady state anthropogenic CO_2 signal on decadal time frames. By embracing more accurate and diverse techniques, we can better help detect how a changing ocean is modifying rising atmospheric CO_2 levels.

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