

Dear Professor Middelburg,

Thank you very much for your attention to this manuscript. As requested, we have thoroughly revised the manuscript in accordance with the reviewer comments (in fact we did this already as soon as the comments were posted).

We have considered the reviewer comments carefully and responded in full to them below. Our primary changes have been to: (1) clarify the question of the use of traditional salinity normalization on DIC, (2) shorten the manuscript to reduce the repetition and enhance the readability, and (3) remove the inconsistency in using nitrate and phosphate to calculate different effects on surface (n)DIC. We believe that these changes, together with other suggested edits, have substantially improved the manuscript.

Yours sincerely,

Yingxu Wu and on behalf of all co-authors

Response to Referee#1

General comments:

“A major short-coming of the paper is the use of Equation 5 (Page 5) to normalize DIC. This procedure has been criticised in the past and shown to create artificial variance in DIC and TA distributions (Friis et al. 2003).”

Response: We agree with the referee that the traditional method of salinity normalization can create artificial variance, as argued by Friis et al. (2003), because it attributes all salinity variation to evaporation and precipitation and ignores the influences of riverine input and upwelling from below the lysocline.

However, we excluded regions subjected to significant perturbations from river inputs (the ocean areas most likely to be affected, as suggested by Kang et al. (2013) and Fry et al. (2015)) as described in section 2.1. In addition, no major rivers flow into the Southern Ocean. Therefore this is not a concern for our study.

The influence of upwelling from below the lysocline on DIC salinity normalization is also relatively negligible in our study. We compared values normalized using the Friis et al. (2003) method (taking account of upwelling) to our original values (normalized in the traditional way) and found a maximum difference of 3.5 $\mu\text{mol kg}^{-1}$, which is of the similar magnitude to the uncertainty in DIC measurement (4 $\mu\text{mol kg}^{-1}$) and much smaller than the phenomenon of interest (>100 $\mu\text{mol kg}^{-1}$).

The calculation following Friis et al. (2003) was implemented using an empirical relationship of the form $n\text{DIC} = \frac{\text{DIC}^{\text{meas}} - \text{DIC}^{\text{S}=0}}{S^{\text{meas}}} \cdot S^{\text{ref}} + \text{DIC}^{\text{S}=0}$, where ‘meas’ denotes measured value and ‘ref’ denotes reference. This equation can then be converted into $n\text{DIC} = \frac{\text{DIC}^{\text{meas}}}{S^{\text{meas}}} \cdot S^{\text{ref}} + \text{DIC}^{\text{S}=0} \cdot (1 - \frac{S^{\text{ref}}}{S^{\text{meas}}})$, where the first term on the right side is the equation we used in the manuscript (Equation 5), and the second term on the right side indicates the difference between the traditional salinity normalization and suggested salinity normalization by Friis et al. (2003). Take the Southern Ocean for instance where the

largest upwelling in the world takes place. The magnitude of the difference term (i.e., $\text{DIC}^{S=0} \cdot (1 - \frac{S^{\text{ref}}}{S^{\text{meas}}})$) depends on $\text{DIC}^{S=0}$ and S^{meas} . $\text{DIC}^{S=0}$ is the region-specific term of $S=0$ due to upwelling of deep water which accumulates the remineralized inorganic carbon. Based on the GLODAPv2 database, the average concentration of DIC at depth greater than 500 m (the largest mixed layer depth in winter in the Southern Ocean, Dong et al., (2008)) in the Southern Ocean ($>40^\circ\text{S}$) is $2250 \mu\text{mol kg}^{-1}$, and the average concentration of DIC at surface layer in the Southern Ocean as defined in this study is $2130 \mu\text{mol kg}^{-1}$. As a consequence, upwelling from below the lysocline ($\text{DIC}^{S=0}$) can create the largest DIC difference of $120 \mu\text{mol kg}^{-1}$ (obviously $\text{DIC}^{S=0}$ in the modern surface ocean should be less than $120 \mu\text{mol kg}^{-1}$, otherwise the DIC vertical distribution would be uniform). The difference term $\text{DIC}^{S=0} \cdot (1 - \frac{S^{\text{ref}}}{S^{\text{meas}}})$ is always relatively small because the average measured salinity in the surface Southern Ocean is 34 and the reference salinity is 35 and so their ratio is close to 1.

We added one paragraph to Section 2.2 to explain why this issue is not quantitatively important in our study.

Specific comments:

Page 1 L28: The formulation of the sentence gives the impression that the concept of DIC was defined by Zeebe and Wolf-Gladrow (2001) which is not the case.

Response: To avoid the wrong impression as pointed out by the referee, we removed the reference cited here since the concept of DIC has been defined very well already.

Page 1 L28: You might want to define the * of CO_2^*

Response: Done. Definition of $[\text{CO}_2^*]$ added.

Page 3 L5-13: I suggest to add calcification as a process controlling DIC, as global CaCO_3 production from calcification is estimated at about 1.6 PgC/yr (Balch et al. 2007), nearly equivalent to the net oceanic sink of atmospheric CO_2 .

Response: Done. We added “production and export of CaCO_3 ” to be another process directly changing the surface distribution of DIC.

Page 4 L17: The formulation of the sentence gives the impression that the Mediterranean is “heavily influenced by river inputs”. The Mediterranean Sea itself is an evaporative basin, with a salinity around 38 higher than the one of the North Atlantic. Only the Black Sea is “heavily influenced by river inputs”.

Response: Corrected. Moved “the Mediterranean Sea” to the next line.

Page 7 L16: I think “organic matter burial” is more adequate than “organic matter sinking to the seafloor”

Response: Changed.

Page 8 Equation 10: Shouldn’t you normalize to a constant salinity Alk_{surf} and $\text{Alk}_{\text{supply}}$ prior to the calculation? Rain or evaporation will change Alk_{surf} this will lead to a deviation from $\text{Alk}_{\text{supply}}$ generating a value for $\text{Alk}_{\text{CaCO}_3}$ even in absence of actual calcification.

Response: The calculation of Alk^* in this manuscript followed Fry et al. (2015), which is already salinity-normalized to a constant salinity of 35. The $\text{Alk}^*_{\text{surf}}$ in Equation 10 was calculated by Equation 11. We added a sentence for clarification.

Page 8 Equation 10: similarly Alk_surf should be corrected for the assimilation of NO₃ and PO₄ by primary production prior to the computation of Alk_CaCO₃. Assimilation of inorganic nutrients by primary production leads to an increase of Alk_surf compared to Alk_supply (Brewer & Goldman 1976) that might obscure the actual signal from calcification.

Response: We agree with the referee that the assimilation of inorganic nutrients by primary production leads to an increase of Alk_{surf}^{*}. We ignored this process previously because the effect of primary production on TA is much smaller than that on DIC (TA:DIC via primary production = -17/106, Wolf-Gladrow et al., 2007). We now modified Equation 10 with a new term to account for the change in TA from photosynthesis or respiration. The latest calculated short-term effect of upwelling (revised Figure 8) is slightly different from the previous version.

Page 9: I do not understand how you accommodate equations 12 and 16 in your model. Equation 12 also accounts for NCP effect on DIC, so that if PO₄ is exhausted this equation allows to compute for “unused DIC”. If Fe is the limiting (micro)-nutrient for primary production then this should lead to “unused PO₄” and allow to compute “unused DIC” also from equation 12.

In addition, the authors preferred instead to use “unused nitrate” because “phosphorus has greater plasticity than nitrogen in plankton stoichiometry”. Then this same reason should apply to compute the effect of NCP on DIC and prohibit the use of phosphate in equation 12, and nitrate should be preferred in equation 12.

For the sake of conceptual consistency in the approach it would be advisable that the effect of DIC assimilation by primary producers and NCP is computed in a consistent way independently of macro/micro nutrient limiting primary production.

Response: We thank the referee for pointing out the inconsistency in calculating NCP effect on DIC and calculating “unused DIC”. We therefore decide to use phosphate as the only nutrient in Equation 12 and 16 in the revised version.

References

- Dong, S., Sprintall, J., Gille, S. T., and Talley, L.: Southern Ocean mixed-layer depth from Argo float profiles, *Journal of Geophysical Research: Oceans*, 113, C06013, [10.1029/2006JC004051](https://doi.org/10.1029/2006JC004051), 2008.
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- Wolf-Gladrow, D. A., Zeebe, R. E., Klaas, C., Körtzinger, A., and Dickson, A. G.: Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, *Marine Chemistry*, 106 (1-2), 287-300, <http://doi.org/10.1016/j.marchem.2007.01.006>, 2007.

Response to Referee#2

General comments:

Since the study is based on the normalization of DIC I'm wondering about the used normalization. It was shown that an easy division by salinity is problematic especially in a global perspective. The authors should validate their approach or at least discuss its problems.

Response: We understand that the referee is concerned that the traditional salinity normalization would create artificial variance as argued by Friis et al. (2003), because the traditional calculation ignores the influences of riverine input and upwelling from below the lysocline.

This issue was addressed in our reply to Referee#1 (<https://www.biogeosciences-discuss.net/bg-2018-376/bg-2018-376-AC1-supplement.pdf>, or see above). We added one paragraph to Section 2.2 to explain why this issue is not quantitatively important in our study.

General comments:

The authors use the GLODAP v2 dataset for the surface ocean. During their calculations they convert data several times into pCO₂. I'm wondering if the use of SOCAT as a pure surface ocean data set might be useful in order to check the calculations.

Response: We did not use SOCAT to check the calculation because it cannot provide a point by point comparison (SOCAT sampling points were at different times and places than GLODAPv2 sampling points).

Takahashi et al. (2014) found good agreement between calculated variables of the carbonate system (e.g., TA, DIC, pCO₂) compared to measured values. Values agreed within the measurement uncertainties assumed for the LDEO database. They found “the computed pCO₂ values from the TCO₂ and TA data are in agreement with the measured values within ±6.8 μatm”. We added one sentence in Section 2.4.1 about this issue.

General comments:

What is with seasonality? Are the authors using seasonal average?

Response: We did not discuss seasonality in the text because this is not the aim of this manuscript, and seasonal changes are of a much lower magnitude than the latitudinal gradient. For instance, the seasonal difference in DIC at the KERFIX site in the Southern Ocean was measured to be 25 μmol kg⁻¹ (Louanchi et al., 1999), which is much less than the overall latitudinal gradient we are looking to explain, of order 200 μmol kg⁻¹.

In addition, in general GLODAPv2 does not contain enough data to constrain seasonal cycles, particularly in the Southern Ocean where winter data is scarce.

General comments: I want to suggest merging the discussion and results sections. There are a lot of parameters discussed and described. Streamlining the sections and shorten it might help the readability. The whole manuscript is not easy to read. This is partly just to the fact that a lot of conversions are done and the reader had to keep track of it. There is not much that can be done to this.

But the authors should carefully proof read their manuscript as some phenomena are discussed in several different positions of the manuscript. Again I want to advocate shortening it where possible in order to improve the readability. Some formulations sound odd and sometimes it's going back and forth especially in the introduction section.

Response: We thank the referee for providing insights into how to improve the readability. In addition to the specific places where repetitions were found by the referee, we also shortened and modified the text (e.g. changes made in Section 1, Section 2.4, and Section 4.1) to avoid repetition and be clearer. However, we decided not to merge the results and discussion sections because it would lead to some very long sub-sections, which in our view would be off-putting to some readers and make the manuscript less rather than more readable.

Specific comments (pp/ll):

01/24: cite the most actual GCB from 2017 or even 2018.

Response: Changed.

01/29: I'm not sure, but is it worth to explain what CO₂* is?

Response: We added an explanation.

02/31 – 03/03: the authors discuss Takahashi (2014) work on page 2. On page 3 they say “since these studies the database was extended: : :”. This doesn't make sense.

Response: We thank the referee for pointing out this issue. We have revised the sentence.

03/12: “other processes” sounds very broad. Can you specify?

Response: We have modified the text to read “the above processes (1-4) which affect TA simultaneously”.

03/14-16: repetition from before 03/18-20: Repetition from before.

Response: 03/14-16 actually summarizes the novelty, which we think is important to retain in order to give the readers a straightforward view of what is new about this study. 03/18-20 was removed, along with 03/20-22.

04/13: I prefer “water depth” over “seafloor depth”.

Response: Changed.

04/25ff: Do the authors take spatial variability of atmospheric CO₂ into account?

Response: We used the globally averaged atmospheric CO₂. We now state this.

04/29: what is xCO₂air? Please explain.

Response: We explained in 04/27 where this term first appears. xCO_{2,air} refers to the atmospheric mole fraction of CO₂. We added an explanation after Equation 2.

05/1-11: Somehow I got confused. It's a lot of steps for a quite easy process. But right now I also don't have a better solution. Just wanted to mention my first thought.

Response: The principle here is we assumed that sea surface CO₂ changes ($\Delta x\text{CO}_{2,\text{sw}}$) track atmospheric CO₂ changes ($\Delta x\text{CO}_{2,\text{air}}$). Then $\Delta x\text{CO}_{2,\text{sw}}$ was converted into ΔDIC using CO₂SYS. We have made a couple of small changes that hopefully reduce confusion.

05/22ff: The formulation is odd. The authors state that they discuss the results in order of their hypotheses with exemptions. There are only three hypotheses so that sentence doesn't make sense to me.

Response: We wanted to discuss the processes step by step. The second hypothesis can be assessed by salinity normalization so we did not have to repeat the analysis. We modified the text to be more clear.

06/10ff: The authors mention that the increased pCO₂ has the potential to elevate values above atmospheric level. But it also can just lower the gradient if seawater is undersaturated.

Response: We agreed with the referee. This paragraph was just to give an explanation of how temperature changes (we used sea water warming as an example) alter the air-sea CO₂ gas exchange and therefore sea surface pCO₂ and DIC. We used the word "potentially" to indicate that this is just one possibility, which sounds most understandable to readers.

07/03: " : : Antarctic Circumpolar Current (ACC): : : "

Response: Changed.

07/05: The term "L3" is not introduced.

Response: We defined L3 in the caption of Figure 4 and now cite that figure.

07/25: One example of not thoroughly structured the document. The authors talk about phosphorus and Redfield. They don't give a number nor a reference. This comes with part of the discussion here later. Please merge.

Response: The number and reference were given after Equation 12 when it came into the calculation of nDIC_{surf}. We moved the number and reference for R_{C:P} from 08/08 to 07/25.

07/33: Do you mean equation 10?

Response: We thanked the referee for pointing out the mistake. Changed.

08/07: Together with Eq. 9 it reduces to nDIC_{surf} = nDIC_{supply} – NCP – 0.5xALK*CaCO₃.

Response: Changed.

08/09: RC should be RC:P.

Response: Changed.

08/11: reference to Figure 5b is 5c.

Response: Changed.

08/12ff: Presenting all the values in a table might be easier to read.

Response: We have already got 4 tables and 10 figures, therefore we decided to keep these values in the text.

08/28: the effect has the potential to lower seawater pCO₂ below atmospheric values.

Response: Changed.

09/32: Why are you not using the nitrate values from GLODAP?

Response: Because GLODAPv2 has sparse observations in the Southern Ocean. For this reason we used the global gridded product based on the WOA dataset. This much larger dataset is available for phosphate but not for DIC or TA. In response to a comment from referee#1, we decided in any case to use the phosphate rather than the nitrate data from WOA in order to be consistent with the calculation for NCP in Equation 9.

11/01: Is evaporation only happening in the Atlantic?

Response: No, the main reason is the very large water vapour transport across Central America, due to the prevailing wind direction towards the west. To avoid giving a misleading impression, we removed the phrase “due to the intense evaporation in the subtropical Atlantic Ocean”.

11/15: Why is $nDIC_{temp}$ the gas exchange effect? Can you explain?

Response: $\Delta nDIC_{temp}$ is analogous to ΔDIC_{temp} , which is defined in equation 8 (Section 2.4.1), It is a measure of the temperature-driven gas exchange effect because it is the difference between $nDIC$ at in-situ temperature and $nDIC$ at 27C. We have added a citation of equation 8 to clarify. As explained in section 2.4.1: “air-sea CO_2 gas exchange was assumed to proceed until pCO_2 was back to the same level as before resetting the temperature.”

17/17ff: CDIAC is no longer maintained.

Response: Changed.

References

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What drives the latitudinal gradient in open ocean surface dissolved inorganic carbon concentration?

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Abstract. Previous work has not led to a clear understanding of the causes of spatial pattern in global surface ocean DIC, which generally increases polewards. Here, we revisit this question by investigating the drivers of observed latitudinal gradients in surface salinity-normalized DIC (nDIC) using the Global Ocean Data Analysis Project Version 2 (GLODAPv2) database. We used the database to test three different hypotheses for the driver producing the observed increase in surface nDIC from low to high latitudes. These are: (1) sea surface temperature, through its effect on the CO₂ system equilibrium constants, (2) salinity-related total alkalinity (TA), and (3) high latitude upwelling of DIC- and TA-rich deep waters. We find that temperature and upwelling are the two major drivers. TA effects generally oppose the observed gradient, except where higher values are introduced in upwelled waters. Temperature-driven effects explains the majority of the surface nDIC latitudinal gradient (182 out of 223 $\mu\text{mol kg}^{-1}$ in the high-latitude Southern Ocean). Upwelling, which has not previously been considered as a major driver, additionally drives a substantial latitudinal gradient. Its immediate impact, prior to any induced air-sea CO₂ exchange, is to raise Southern Ocean nDIC by ~~208-220~~ $\mu\text{mol kg}^{-1}$ above the average low latitude value. However, this immediate effect is transitory. The long-term impact of upwelling (brought about by increasing TA), which would persist even if gas exchange were to return the surface ocean to the same CO₂ as without upwelling, is to increase nDIC by 74 $\mu\text{mol kg}^{-1}$ above the low latitude average.

1 Introduction

The ocean absorbs about one quarter of the anthropogenic CO₂ emitted every year (Le Quéré et al., ~~2015~~2018). It is the largest non-geological carbon reservoir (~38000 Gt C) (Falkowski et al., 2000), containing 50 times as much carbon as the pre-industrial atmosphere, and thereby plays an important role in modulating the Earth's climate system. Approximately 97% of the oceanic carbon pool exists in the form of dissolved inorganic carbon (DIC) (Falkowski et al., 2000), which is defined as the sum of the concentrations of aqueous CO₂, bicarbonate and carbonate ions (~~Zeebe and Wolf Gladrow, 2001~~):

$$\text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$

30 where $[\text{CO}_2^*]$ refers to the sum of aqueous CO₂ and true carbonic acid (H₂CO₃), with the latter negligible (Zeebe and Wolf-Gladrow, 2001).

Understanding the distribution of DIC in seawater is essential for understanding anthropogenic CO₂ invasion (Gruber, 1998; Humphreys et al., 2016; Lee et al., 2003; Sabine et al., 1999; Sabine et al., 2002; Vázquez-Rodríguez et al., 2009) and ocean acidification (Doney et al., 2009; Orr et al., 2005). Given that the surface ocean is where most organisms live, and that it is the part of the ocean that exchanges CO₂ with the atmosphere, the controls on surface DIC particularly merit investigation. ~~This is the topic that we address in this paper, giving particular attention to the question of what sustains the high DIC concentrations observed in the Southern Ocean, given that region's crucial role in the global overturning circulation (e.g., Marshall and Speer, 2012), deep water formation (e.g., Orsi et al., 1999) and the global carbon cycle (Caldeira and Duffy, 2000; Landschützer et al., 2015; Marinov et al., 2006; Mikaloff Fletcher, 2015; Takahashi et al., 2012).~~

Many previous studies focused on the vertical rather than the horizontal distribution of DIC, aiming to understand the relative contributions of the different “carbon pumps” in controlling DIC variations throughout the water column (i.e., solubility pump, soft tissue pump, and carbonate pump, see details in Cameron et al., 2005; Gruber and Sarmiento, 2002; Toggweiler et al., 2003a; Toggweiler et al., 2003b). However, the solubility pump is so named because it is based on an assumption about the horizontal distribution of surface DIC – that DIC is high where new deep waters form at high latitudes, because of the effect of temperature on CO₂ solubility.

Previous work on the horizontal distribution of surface DIC included development of an algorithm to approximately reproduce the global surface DIC distribution (Lee et al., 2000), in which salinity-normalized DIC (nDIC) was predicted from empirically-derived functions of sea surface temperature and nitrate that varied seasonally and geographically. Key et al. (2004) depicted the global distribution of surface DIC based on an earlier version (GLODAPv1) of the dataset used here, noting that the surface DIC pattern is overall more similar to nutrients (including in the Southern Ocean, where both DIC and nutrients are enriched) than to salinity, unlike total alkalinity (TA) whose pattern more closely resembles that of salinity (Fry et al., 2015). Using the data from the new GLODAPv2 database (Key et al., 2015; Olsen et al., 2016), surface DIC is confirmed here to have its highest values at high latitudes, like nutrients, and to reach its lowest values in the equatorial zone in each basin (Fig. 1a; more details in Sect. 3.1). Earlier studies (Lee et al., 2000; Toggweiler et al., 2003a; Williams and Follows, 2011, Sect. 6.3 “What controls DIC in the surface ocean?”) suggested that temperature is of primary importance in regulating surface DIC; under this assumption, surface waters in cool regions at high latitudes should hold more DIC than surface waters in the warm regions at low latitudes (Williams and Follows, 2011, Toggweiler et al., 2003a). Temperature may also drive latitudinal differences in carbonate ion concentration and surface aragonite saturation state (Ω_{arag}) (Jiang et al., 2015; Orr et al., 2005), through its effect on CO₂ solubility and CO₂ system thermodynamics.

Unlike previous studies, Williams and Follows (2011) argued that another variable also exerts a secondary control on the surface DIC distribution: at a given DIC, TA influences the seawater partial pressure of carbon dioxide (see also Omta et al., 2011), and therefore air-sea gas exchange. Takahashi et al. (2014) subsequently explored the seasonal climatological distributions of surface DIC using seawater $p\text{CO}_2$ from the Lamont Doherty Earth Observatory (LDEO) database and TA estimated from sea surface salinity, qualitatively attributing seasonal differences (on a regional scale) to the greater upward mixing of high-CO₂ deep waters in winter and summer biological carbon drawdown. Their study pointed out the great potential

of upwelling to alter surface DIC, but it was focused more on controls on DIC seasonality rather than DIC spatial variability. ~~In recent years, Since these studies,~~ the global surface DIC database has been greatly expanded (~~e.g., Bates et al., 2006; Sasse et al., 2013; Takahashi et al., 2014~~), culminating now in GLODAPv2 (Key et al., 2015; Olsen et al., 2016), but the controls producing the global spatial DIC distribution have not been quantitatively reassessed.

5 Many processes are known to influence the sea surface distribution of DIC at the local scale. They can be divided overall into those which change DIC concentration by direct addition or removal (e.g., ~~1 and 2-1-3~~ of the following), and those which affect DIC indirectly (e.g., ~~3-4-5-6~~ of the following): (1) biological carbon assimilation during primary production and releasing during remineralization (Bozec et al., 2006; Clargo et al., 2015; Toggweiler et al., 2003b; Yasunaka et al., 2013); (2) transport of DIC-rich deep waters into the surface layer (Jiang et al., 2013; Lee et al., 2000); ~~(3) production and export of CaCO₃; (3-4)~~ seawater dilution/concentration due to precipitation/evaporation (Friis et al., 2003); ~~(4-5)~~ warming or cooling, which alters the CO₂ solubility and induces air-sea gas exchange that acts to reduce air-sea CO₂ disequilibrium (Bozec et al., 2006; Toggweiler et al., 2003a; Williams and Follows, 2011); and ~~(5-6) other the above processes (1-4) which affect through their on~~ TA: if high/low TA values are not matched by high/low DIC values then the resulting low/high seawater *p*CO₂ stimulates ingassing/outgassing until DIC matches TA (Humphreys, 2017).

15 Our study differs from previous work in several ways. Firstly, whereas many previous studies looked to understand the vertical DIC distribution, here the target is to understand the horizontal surface DIC distribution. Secondly, we look to identify the most important *processes* not just *variables* driving the surface distribution (Fig. 2). Another difference from previous studies is our use of a much larger observational global dataset – GLODAPv2.

~~The general consensus from previous work has been that the global pattern of sea surface temperature (SST) dominates the latitudinal distribution of surface DIC (Williams and Follows, 2011). More recently, TA has also been considered important (Omta et al., 2011; Williams and Follows, 2011). We reassess this topic by quantitatively investigating the importance of SST to surface DIC and its primary controls (heating and cooling), and TA (evaporation and precipitation, Fry et al., 2015), and also the effect of high latitude upwelling. A novel conclusion of this study is that the latter process, whose global significance has previously been overlooked, is also very important in shaping the spatial distribution of surface ocean DIC.~~

25 We ~~therefore~~ evaluated the following three main hypotheses as to which processes cause the increase in surface DIC and nDIC from low to high latitudes (Fig. 1):

- (1) latitudinal variation of solar heating via its effect on sea surface temperature, and hence CO₂ solubility;
 - (2) evaporation and precipitation, through their effects on TA; and
 - (3) upwelling and winter entrainment through the introduction of DIC- and TA-rich deep waters to the (sub)polar surface
- 30 oceans, when coupled with iron limitation of biological uptake of DIC.

It is easier to constrain the dynamics of upwelling and quantify its impact on surface DIC in the Southern Ocean (where upwelling has been more comprehensively studied, e.g., Marshall and Speer, 2012; Morrison et al., 2015) than in the subarctic North Atlantic and North Pacific Oceans (where upwards transport occurs via deep mixing in the winter, combined with upwelling in the North Pacific). The Southern Ocean also plays a crucial role in the global overturning circulation (e.g.,

Marshall and Speer, 2012), and the global carbon cycle (Landschützer et al., 2015; Mikaloff-Fletcher, 2015). Therefore, we focused on the Southern Ocean for the evaluation of the third hypothesis.

The processes that we evaluated can be separated into two categories: equilibrium and disequilibrium processes (Fig. 2). The effects of equilibrium processes (the effects through temperature and upwelled TA) change the surface ocean DIC at which air-sea CO₂ equilibrium would occur, and those effects can therefore persist beyond the air-sea CO₂ equilibrium timescale (months to year, Jones et al., 2014). The effects of disequilibrium processes (the effects through direct supply of DIC from upwelling and the effects through biological uptake of DIC in response to upwelled nutrients (principally iron, Moore et al., 2016)), on the other hand, are likely to persist only over timescales shorter than the CO₂ equilibrium timescale. A novel conclusion of this study is that upwelling, whose global significance has previously been overlooked, is very important in shaping the spatial distribution of surface ocean DIC, in part because upwelling of TA changes equilibrium DIC.

2 Methods

Data for this study were taken from GLODAPv2 (<https://www.nodc.noaa.gov/ocads/oceans/GLODAPv2/>/<http://ediac.ornl.gov/oceans/GLODAPv2/>) (Key et al., 2015; Olsen et al., 2016). This product includes data from over 700 cruises conducted during the years 1972-2013 with a large fraction (~34%) having taken place during the period 2003-2013. These data have been subject to secondary quality control and subsequent adjustments (Key et al., 2015; Lauvset and Tanhua, 2015; Olsen et al., 2016). We define the surface ocean as waters shallower than 30 m at latitudes greater than 30°, and shallower than 20 m at latitudes less than 30° (following e.g., Fry et al., 2015; Lee et al., 2006). Only open ocean data (~~seafloor-water~~ depth > 200 m) were included in this study (Fig. 3).

2.1. Data processing

We excluded regions subjected to significant perturbations from river inputs in order to remove confounding factors affecting the latitudinal distributions of DIC and nDIC on smaller length scales than being investigated here. ~~To this end, w~~We excluded all data from the ~~Mediterranean Sea and~~ Arctic Ocean (> 65° N) (Fig. 3) because they are heavily influenced by river inputs (Fry et al., 2015; Jiang et al., 2014), all data from the Mediterranean Sea and the Red Sea because of its very high salinity (Jiang et al., 2014), as well as some data (those where S is less than 34) from other ocean areas: the Amazon River plume in the North Atlantic (5° N-10° N, > 45° W), the Ganges/Brahmaputra plume in the Bay of Bengal (> 5° N, 80-94° E) (both Fry et al., 2015) and the western North Atlantic margins (Cai et al., 2010). We also excluded relatively small low-latitude ocean areas affected by upwelling (the eastern equatorial Pacific and northern Californian upwelling regions).

Because atmospheric CO₂ increased during the time that the GLODAPv2 data was collected (1972-2013), DIC has also increased in response in surface ocean waters (Bates et al., 2014). To prevent DIC time trends from generating artificial spatial variability, we normalized surface DIC to a reference year of 2005. We assumed that sea surface CO₂ changes track atmospheric CO₂ changes (Feely, 2008; see also CO₂ Time Series in the North Pacific at

<https://pmel.noaa.gov/co2/file/CO2+time+series>). We first calculated the change of atmospheric mole fraction of CO₂ ($x\text{CO}_{2,\text{air}}$) from the reference year 2005:

$$\Delta x\text{CO}_{2,\text{air}} = x\text{CO}_{2,\text{air}}^t - x\text{CO}_{2,\text{air}}^{2005} \quad (2)$$

where the superscript “t” and “2005” refer to year, and the globally averaged atmospheric xCO₂ data can be found at

5 <https://www.esrl.noaa.gov/gmd/ccgg/trends/> (neither spatial nor seasonal variability in atmospheric CO₂ is taken into account).

Then we converted $\Delta x\text{CO}_{2,\text{air}}$ into $\Delta p\text{CO}_{2,\text{air}}$ (Takahashi et al., 2009) just above the sea surface, using in-situ hydrological humidity data from sea surface water. It is then assumed that $\Delta p\text{CO}_{2,\text{sw}}$, representing the change of sea surface pCO₂ relative to the year 2005, is equal to $\Delta p\text{CO}_{2,\text{air}}$.

Therefore the calculation of the sea surface pCO₂ normalized to year 2005 refers to was calculated as:

$$10 \quad p\text{CO}_{2,\text{sw}}^{2005} = p\text{CO}_{2,\text{sw}}^t - \Delta p\text{CO}_{2,\text{sw}} \quad (3)$$

where $p\text{CO}_{2,\text{sw}}^t$ was calculated from in-situ DIC, TA, temperature and salinity through CO₂SYS (van Heuven et al., 2011; dissociation constants used are described in Sect. 2.3).

Since the anthropogenic CO₂ perturbation does not change TA, DIC normalized to 2005 was calculated with inputs of in-situ TA and $p\text{CO}_{2,\text{sw}}^{2005}$ using CO₂SYS (van Heuven et al., 2011):

$$15 \quad \text{DIC}^{2005} = f(T_{\text{in-situ}}, S_{\text{in-situ}}, \text{TA}_{\text{in-situ}}, p\text{CO}_{2,\text{sw}}^{2005}) \quad (4)$$

The concentration of DIC hereinafter refers to the DIC normalized to year 2005.

2.2 Salinity normalization

Salinity normalization was used to correct for the influence of precipitation and evaporation in the open ocean (Postma, 1964).

Data were normalized to a reference salinity of 35 using a standard procedure:

$$20 \quad nX = X_{\text{obs}} \times 35/S_{\text{obs}} \quad (5)$$

where nX refers to the normalized variable, X_{obs} is the observed value of the variable, and S_{obs} is the observed salinity.

It should be acknowledged that straightforward salinity normalization (Eq. 5) can create artificial variance in DIC distribution (Friis et al., 2003) because it ignores the influences of riverine input and upwelling from below the lysocline. To this end, we excluded the major regions affected by river inputs (see text in Sect. 2.1). In addition, we found that the influence of upwelling from below the lysocline on salinity normalization of DIC is negligible (i.e., it can only account for up to 4 $\mu\text{mol kg}^{-1}$ artificial change in DIC) compared with the DIC latitudinal gradient of about 200 $\mu\text{mol kg}^{-1}$ that we seek to explain in this study.

25

2.3 Carbonate chemistry

Carbonate system variables were calculated from DIC and TA using version 1.1 of CO₂SYS for MATLAB (van Heuven et al., 2011). The dissociation constants for carbonic acid and sulfate were taken from Lueker et al. (2000) and Dickson (1990),

30 respectively, and the total borate-salinity relationship from Lee et al. (2010).

2.4 Calculations of the effects of various processes on DIC

~~The second hypothesis (evaporation and precipitation through their effects on TA) was evaluated by salinity normalization (Eq. 5). The methods for calculating the impacts of different the other two processes on the surface DIC concentration are now explained in the order of hypotheses proposed, except for the second hypothesis (evaporation and precipitation through their effects on TA) which was evaluated by salinity normalization. The underlying purpose in each case is to better understand how the observed low to high latitude gradients in (n)DIC are produced.~~ The effect of upwelling is evaluated in the Southern Ocean, from both short- and long-term perspectives. In addition, we also quantify the effect of iron limitation, which would potentially affect the observed (n)DIC distribution.

2.4.1 SST-driven effect

10 Generally, the temperature effect on the carbonate system has two aspects. Firstly, when water temperature increases, the equilibrium between carbonate species (Eq. 6) shifts to the left, increasing the aqueous CO₂ and carbonate ion concentrations (Dickson and Millero, 1987):



Secondly, CO₂ solubility is reduced at higher temperatures and vice versa (Weiss, 1974). Neither effect alters DIC directly but
15 both lead to changes in *p*CO₂. A larger proportion of DIC exists as aqueous CO₂ at higher temperatures and the ratio of *p*CO₂ to [CO₂] also increases as solubility decreases (Eq. 7, Henry's Law):

$$p\text{CO}_2 = [\text{CO}_2]/K_H \quad (7)$$

where *K_H* is the Henry's constant (solubility) for CO₂, one of the CO₂ system equilibrium constants.

Both effects thus tend to increase sea surface *p*CO₂ as sea water warms, potentially elevating it to values above the atmospheric
20 *p*CO₂ and thereby stimulating air-sea CO₂ gas exchange; the induced outgassing of CO₂ reduces sea surface CO₂ and DIC as it shifts the system towards air-sea CO₂ equilibrium. Therefore, for an open ocean system with gas exchange with the atmosphere, the DIC distribution has the potential to be controlled by the SST distribution, and this can by itself produce DIC latitudinal variations.

To examine the magnitude of the expected temperature-induced DIC changes, we chose the low-latitude area as the reference,
25 then removed the latitudinal SST variation and recalculated the open ocean surface DIC everywhere for a constant SST of 27°C (the mean sea surface temperature in the subtropics 30° S-30° N). To do this we first calculated the in-situ *p*CO₂ from observed SST, SSS (sea surface salinity), TA and DIC using CO₂SYS. The calculated *p*CO₂ from TA and DIC has been found to agree well with the measured *p*CO₂ (root mean square deviation of ± 6.8 μatm, Takahashi et al., 2014). We then altered the sea surface temperature from its in-situ value to 27°C, which would change the solubility of CO₂ and induce air-sea CO₂ gas
30 exchange. Then air-sea CO₂ gas exchange (which does not change TA) was assumed to proceed until *p*CO₂ was back to the same level as before resetting the temperature. Next, we used CO₂SYS to calculate DIC_{SST=27} based on an input temperature of 27°C, observed salinity and TA, and the in-situ *p*CO₂ calculated as above. DIC_{SST=27} thus represents temperature-normalized

DIC, and should exhibit the same spatial variability as DIC except that the temperature-induced component of the variability has been removed. Finally, the difference between observed DIC and $DIC_{SST=27}$ gives the DIC variation attributed to temperature variation:

$$\Delta DIC_{temp} = DIC_{obs} - DIC_{SST=27} \quad (8)$$

5 2.4.2. Upwelled DIC-driven effect (short-term effect of upwelling)

Upwelling of DIC-rich subsurface water is capable of increasing the surface DIC. The largest upwelling (in terms of flow rate) anywhere in the world takes place in the Southern Ocean (Talley, 2013): the upwelling there is made up of 18 Sv (Sverdrup, 1 Sv = $10^6 \text{ m}^3/\text{s}$) of NADW (North Atlantic Deep Water), 11 Sv of IDW (Indian Deep Water), and 9 Sv of PDW (Pacific Deep Water). Subsurface waters in the Southern Ocean are considered to upwell along the neutral density isopycnals of 27.6 kg m^{-3} , 27.9 kg m^{-3} and 27.9 kg m^{-3} in the southern Atlantic, Indian and Pacific Oceans, respectively (Ferrari et al., 2014; Lumpkin and Speer, 2007; Marshall and Speer, 2012; Talley, 2013).

Upwelling occurs within the ACC (Antarctic Circumpolar Current (ACC)) at those latitudes where the wind stress is greatest (Morrison et al., 2015); as the upwelled water subsequently advects away, the effects are transported to nearby locations. Therefore, instead of a direct supply from deep to surface locations such as L3 (Fig. 4), DIC is assumed to be brought to the subsurface primarily along isopycnals (shown in Fig. 4 as the black curve to L1), finally reaching the surface at L2, the zone in which upwelling occurs. Then, the upwelled subsurface water with enriched DIC, TA and nutrients feeds both branches of the overturning in the Southern Ocean. One is transported northwards via Ekman transport from L2 to L3 to join the upper branch, as shown by the black arrow towards the equator, and the other one is recycled back through the lower branch to form Antarctic Bottom Water (AABW) (Talley, 2013). Potential effects of upwelling on sea surface temperature are not considered here, but are likely to be small because both deep water and high-latitude surface waters are cold.

We first consider the increase in DIC induced by the upwelling of deep water with high DIC concentrations. While some of the initial increase is usually removed shortly afterwards by biological export fueled by the nutrients brought up at the same time, excess DIC remains if the subsequent biological removal of DIC does not match the initial increase. Phosphorus has the simplest nutrient behavior in the ocean with only one significant source to the ocean as a whole (river input) and one major sink (organic matter ~~sinking to the seafloor~~ burial) (Ruttenberg, 2003; Tyrrell, 1999). In this study, the salinity-normalized phosphate (nPhos) concentration was used as a proxy for calculating how much salinity-normalized DIC (nDIC) was upwelled along with it and not yet removed again by biological uptake of phosphate and DIC. We used salinity-normalized concentrations to correct for the influence of precipitation (rainfall) that dilutes DIC and phosphate concentrations in proportion to the effects on salinity (Eq. 5). In this calculation, it was assumed that the only external source of phosphate to surface waters is from upwelling and the only subsequent loss is through export of organic matter, leading to the equation:

$$nPhos_{surf} = nPhos_{supply} - NCP/R_{C:P} \quad (9)$$

where the subscript ‘supply’ indicates the end-member concentration of deep water supplied along the upwelling isopycnals (i.e., the value at L1 in Fig. 4), and the subscript ‘surf’ indicates the surface water concentration at some later time. NCP refers

to the total time-integrated net community production (uptake and export by biology) in carbon units, and $R_{C:P}$ is the Redfield ratio of carbon to phosphorus. $R_{C:P}$ is given the standard value of 106:1 (Redfield, 1963), except for the cold nutrient-rich high-latitude region in the Southern Ocean (south of 45° S), where $R_{C:P}$ is given a lower value, of 78:1 (Martiny et al., 2013). $nPhos_{surf}$ refers to the observed surface value of $nPhos$ at some location distant from where upwelling occurs.

- 5 Another possible process involved in the change of DIC during its upwelling and subsequent advection is calcium carbonate ($CaCO_3$) precipitation and dissolution (Balch et al., 2016), which alters DIC and TA with a ratio of 1:2. In order to quantify the magnitude of this process, we used Alk^* (Fry et al., 2015) as an indicator, which is capable of diagnosing $CaCO_3$ cycling in the context of the large-scale ocean circulation (see more details on Alk^* distribution in Fig. 10). ~~By attributing t~~The change in Alk^* concentrations between its supplied and surface end-members is attributed to $CaCO_3$ precipitation/dissolution and
 10 assimilation of inorganic nutrients by primary production (Brewer and Goldman, 1976), we then calculated $\Delta Alk^*_{CaCO_3}$ (Eq. 11), and converted it to the change in $nDIC$ (i.e., $0.5 \times \Delta Alk^*_{CaCO_3}$):

$$Alk^*_{surf} = Alk^*_{supply} - \Delta Alk^*_{CaCO_3} - NCP/R_{DIC:TA} \quad (10)$$

$$Alk^* = \frac{Alk_m - Alk_r + 1.36 \times NO_3^-}{S} \times 35 + Alk_r - 2300 \mu mol kg^{-1} \quad (11)$$

- where $R_{DIC:TA}$ is the relative ratio of -106/17 between changes in DIC and TA during primary production (Wolf-Gladrow et
 15 al., 2007). Alk_m is the measured TA, Alk_r is the riverine TA end-member (zero in the Southern Ocean), and $2300 \mu mol kg^{-1}$ is the average TA in the low-latitude surface oceans. Alk^*_{surf} is calculated by Eq. 11.

Assuming the carbon source is from upwelled CO_2 -rich deep waters and carbon sinks are from organic matter export (NCP) and $CaCO_3$ cycling, then:

$$nDIC_{surf} = nDIC_{supply} - \left(\frac{nPhos_{supply} - nPhos_{surf}}{R_{C:P}} \right) \times R_{C:P} NCP - 0.5 \times \Delta Alk^*_{CaCO_3} \quad (12)$$

- 20 $R_{C:P}$ is given the standard value of 106:1 (Redfield, 1963), except for the cold nutrient rich high latitude region in the Southern Ocean (south of 45° S), where R_C is given a lower value, of 78:1 (Martiny et al., 2013).

- Three hydrographic sections, one in each of the Indian (I95E), Pacific (P150W), and Atlantic (A25W) Oceans, were used to determine the different supply concentrations ($nPhos_{supply}$, Alk^*_{supply} and $nDIC_{supply}$) for each basin (see Fig. ~~5b~~ 5c inset, values here are expressed as mean \pm standard error of the mean). In the Indian Ocean, $nPhos_{supply}$, Alk^*_{supply} and $nDIC_{supply}$ along the
 25 27.9 $kg m^{-3}$ isopycnal are $2.29 \pm 0.01 \mu mol kg^{-1}$, $109.4 \pm 1.0 \mu mol kg^{-1}$, and $2273.1 \pm 1.1 \mu mol kg^{-1}$, respectively, as it approaches the surface. In the Pacific Ocean, $nPhos_{supply}$, Alk^*_{supply} and $nDIC_{supply}$ along the 27.9 $kg m^{-3}$ isopycnal are $2.32 \pm 0.01 \mu mol kg^{-1}$, $108.1 \pm 1.9 \mu mol kg^{-1}$, and $2277.2 \pm 1.8 \mu mol kg^{-1}$, respectively. In the Atlantic Ocean, $nPhos_{supply}$, Alk^*_{supply} and $nDIC_{supply}$ along the 27.6 $kg m^{-3}$ isopycnal are $2.28 \pm 0.01 \mu mol kg^{-1}$, $103.5 \pm 1.1 \mu mol kg^{-1}$, and $2254.6 \pm 1.3 \mu mol kg^{-1}$, respectively (Fig. ~~5a~~ 5b).

- 30 Since $nPhos_{surf}$ tends to decrease to zero upon moving northwards, due to biological uptake, $nDIC_{surf}$ has a relatively constant value in the subtropical regions (data not shown), where is not influenced by upwelling in the Southern Ocean. Because of this, the potential effect of upwelling on surface $nDIC$, is calculated as the excess in $nDIC_{surf}$ compared to the subtropical average value (30° S-30° N):

$$\Delta n\text{DIC}_{\text{upw_st}} = n\text{DIC}_{\text{surf}} - \overline{n\text{DIC}_{\text{surf}} (30^\circ \text{S}-30^\circ \text{N})} \quad (13)$$

2.4.3. Upwelled TA-driven effect (long-term effect of upwelling)

Some effects of upwelling on DIC are temporary, becoming overridden later by gas-exchange. In contrast, the effect of upwelled TA persists because it changes the equilibrium DIC with respect to gas exchange (DIC_{eq}) (discussed also in Sect. 4.1.3). Upwelling of high-TA water has a long-lasting effect on DIC because, if all else remains constant, an increase in TA decreases the fraction of DIC that exists as CO_2 molecules. The resulting decrease in CO_2 concentration lowers seawater partial pressure of CO_2 ($p\text{CO}_2$), ~~tending to having the potential to make lower~~ seawater $p\text{CO}_2$ ~~lower to below than~~ atmospheric ~~values~~ $p\text{CO}_2$ which in turn drives an influx of CO_2 from the atmosphere, raising DIC (Humphreys et al., 2017). The effects of upwelling are complex because they consist of both direct and indirect effects on DIC (Fig. 2), lasting over both short (when DIC is altered but DIC_{eq} is not) and long (when DIC_{eq} is altered) timescales. The different effects and the meanings of the terms used here are illustrated in Fig. 6.

The calculation of the long-term effect of upwelling through upwelled TA in the Southern Ocean (i.e., the difference between DIC_3 and DIC_0 in Fig. 6) was achieved through five steps:

(1) calculation of TA in the Southern Ocean with the upwelling effect subtracted, $\text{TA}_{\text{nonupw}}$:

$$\text{TA}_{\text{nonupw}} = \text{TA}_{\text{obs}} - (\text{Alk}^* \times S_{\text{obs}} / 35) \quad (14)$$

where TA_{obs} is the observed in-situ TA, and Alk^* is the TA tracer (Fry et al., 2015) revealing excess TA supplied by the large-scale ocean circulation (upwelling in the Southern Ocean), as well as removal by calcification and export (Eq. 121). Since Alk^* is a salinity-normalized concept, it is necessary to restore it to the in-situ salinity before subtracting it from the in-situ TA.

(2) calculation of in-situ sea surface $p\text{CO}_2$, following the same method as described in Sect. 2.4.2.

(3) calculation of DIC with the effect of upwelled TA subtracted. We calculated $\text{DIC}_{\text{nonupw}}$ using CO_2SYS with inputs of $\text{TA}_{\text{nonupw}}$ and in situ $p\text{CO}_2$, SST and salinity.

(4) salinity-normalization for consistency with other calculated effects.

(5) finally, the long-term effect of upwelling through the upwelled TA and the subsequent air-sea gas exchange is calculated as:

$$\Delta n\text{DIC}_{\text{upw_lt}} = n\text{DIC}_{\text{obs}} - n\text{DIC}_{\text{nonupw}} \quad (15)$$

where $\Delta n\text{DIC}_{\text{upw_lt}}$ corresponds to the magnitude of ⑤ in Fig. 6.

2.4.4. Iron-driven effect

The iron limitation-driven DIC differences ($\Delta\text{DIC}_{\text{Fe}}$) relate to the concepts of “unused nutrient” and associated “unused DIC”, which can be thought of as the amounts of macro-nutrients and DIC that are left behind after iron limitation brings an end to biological uptake, in those regions where iron is the limiting nutrient. Iron limitation alters the impact of upwelling. In locations

experiencing upwelling but where nitrate is the proximate limiting nutrient, then the quantity of upwelled DIC might more or less be balanced by the quantity of subsequently exported DIC (fueled by the upwelled nitrate). In the Southern Ocean, however, the two appear not to be close to balance, even before considering iron limitation. According to the calculations in Sect. 2.4.32, the ratio of the excess upwelled nDIC against nPhos is around 250:2.3 \approx 109:1 for the Southern Ocean, considerably exceeding the low C:P (average \approx 80:1) of organic matter in the region (Martiny et al, 2013). So even if all upwelled phosphate were to be used up and then exported in biomass in conjunction with carbon, a considerable surplus of DIC would be left behind. A lack of iron in surface waters, however, leads to even more upwelled DIC being left behind after the end of blooms induced by the upwelled nutrients.

~~Because phosphorus has greater plasticity than nitrogen in plankton stoichiometry, P:C (i.e. the elemental ratio of phosphorus:carbon) exhibits significantly more variability in the ocean than does N:C (Galbraith and Martiny, 2015). Because of this, we chose in this instance to use nitrate-phosphate as the “unused nutrient” from which to calculate “unused DIC”.~~ For each $1^\circ \times 1^\circ$ grid in the surface open ocean, the unused nitrate-phosphate was taken from its annual minimum concentration based on the monthly data in World Ocean Atlas 2013 version 2 (WOA 2013: <https://www.nodc.noaa.gov/OC5/woa13/>, Boyer et al., 2013). The unused nitrate-phosphate was then converted into unused DIC based on a C:~~N:P~~ ratio of 106:~~16-1~~ (Redfield, 1963) for most of the global ocean, except in the warm nutrient-depleted low-latitude gyres, warm nutrient-rich equatorial upwelling regions, and cold nutrient-rich high-latitude regions. The C:N ratios used for these three regions were 195:~~281~~, 137:~~481~~, and 78:~~131~~, respectively (Martiny et al., 2013).

The amount of unused DIC was therefore calculated as:

$$\text{unused DIC} = \text{unused } \del{\text{nitrate-phosphate}} \times R_{C:\del{NP}} \quad (16)$$

20 2.5. Uncertainty estimation

In this study, uncertainties in calculated effects of different drivers (e.g., $\Delta\text{nDIC}_{\text{temp}}$, $\Delta\text{nDIC}_{\text{upw_st}}$, $\Delta\text{nDIC}_{\text{upw_lt}}$) were determined by a Monte Carlo approach. For example, the uncertainty of $\Delta\text{nDIC}_{\text{temp}}$ was calculated as follows: (1) given that $\Delta\text{nDIC}_{\text{temp}}$ is the difference between nDIC_{obs} and $\text{nDIC}_{\text{SST=27}}$ (Eq. 9), its uncertainty is propagated from the uncertainties of both nDIC_{obs} and $\text{nDIC}_{\text{SST=27}}$, where the uncertainty of nDIC_{obs} is $5 \mu\text{mol kg}^{-1}$ (Table 2), and the uncertainty of $\text{nDIC}_{\text{SST=27}}$ was determined by a Monte Carlo approach; (2) for calculation of the uncertainty of $\text{nDIC}_{\text{SST=27}}$ (see its function in Table 1), we first calculated artificial random errors (normally distributed according to the central limit theorem, with a mean of zero and a standard deviation equal to the accuracy/uncertainty of measurement) using a random number generator. Then, new carbonate system variable values (the original ones plus the randomly generated errors) were input into the CO₂SYS program (Van Heuven et al., 2011) to calculate new $\text{nDIC}_{\text{SST=27}}$ values. By doing this 1000 times, we obtained a set of 1000 different values for every single data point in the dataset. We used the standard deviations of these sets to characterize their individual uncertainties. The overall uncertainty of $\text{nDIC}_{\text{SST=27}}$ was $6.4 \mu\text{mol kg}^{-1}$; (3) by applying the same Monte Carlo method, but to calculate the uncertainty propagated through Eq. (9), we then calculated the uncertainty of $\Delta\text{nDIC}_{\text{temp}}$ to be $8.0 \mu\text{mol kg}^{-1}$ (Table 2).

This Monte Carlo approach has been used previously (e.g., Juranek et al., 2009; Ribas-Ribas et al., 2014) to propagate uncertainties involving CO₂ system calculations.

3. Results

3.1. Spatial distributions of DIC and nDIC

- 5 Surface observations reveal values of DIC across the global ocean ranging from less than 1850 $\mu\text{mol kg}^{-1}$ in the tropics to more than 2200 $\mu\text{mol kg}^{-1}$ in the high latitudes (Fig. 1a). To first order, surface DIC increases polewards, being positively correlated with absolute latitude (Spearman's rank correlation coefficient $\rho = 0.71$ for the global oceans, Table 3). Spatially, it is monotonically inversely related to sea surface temperature ($\rho = -0.78$, Table 3), with DIC being highest where the surface ocean is coolest. Another conspicuous feature of surface DIC is the higher values (by $\sim 100 \mu\text{mol kg}^{-1}$ higher) in the tropical and subtropical Atlantic Ocean relative to the same latitudes in the Pacific and Indian Oceans (Fig. 1a), ~~due to the intense evaporation in the subtropical Atlantic Ocean, as well as attributed to~~ the transport of water vapor from the Atlantic to the Pacific (Broecker, 1989). This is not considered further here because our main purpose is to explain the sizeable observed latitudinal gradients in DIC (on average 153 $\mu\text{mol kg}^{-1}$ higher in the Southern Ocean than at low latitudes, for instance) and nDIC (on average 223 $\mu\text{mol kg}^{-1}$ higher in the Southern Ocean than at low latitudes).
- 10
- 15 Salinity-normalized DIC (nDIC) increases towards the poles in all three ocean basins (Fig. 1b), although less strongly in the North Atlantic. The surface nDIC correlates more tightly with latitude and SST than does DIC, yielding a positive correlation with absolute latitude and a negative correlation with SST ($\rho = 0.86$ and -0.94 respectively for the global ocean, Table 3). The distributions of surface DIC and particularly nDIC also show modest regional maxima in the eastern equatorial Pacific, the Arabian Sea, and the eastern boundaries of the Pacific and Atlantic Ocean basins, presumably as a result of upwelling
- 20 (Capone and Hutchins, 2013; Chavez and Messié, 2009; Millero et al., 1998; Murray et al., 1994).

3.2. SST-driven effect in the global surface ocean

- The differences between the latitudinal patterns of DIC_{obs} and $\text{DIC}_{\text{SST}=27}$ are shown in Fig. 7. As expected, $\text{DIC}_{\text{SST}=27}$ agrees well with DIC_{obs} in the subtropics where SST is close to 27°C; the differences become larger with increasing latitude and decreasing SST (Fig. 7a-c). Correcting for salinity variations (Fig. 7d-f) greatly reduces the variability in DIC at low latitudes:
- 25 nDIC_{obs} is fairly constant at $\sim 1970 \mu\text{mol kg}^{-1}$ in the subtropics. $\Delta\text{nDIC}_{\text{temp}}$ (Eq. 8 but for nDIC), the temperature-driven CO₂ gas exchange effect on surface nDIC, increases sharply with latitude (Fig. 7g-i), reaching $\sim 220 \mu\text{mol kg}^{-1}$ at 70° S, and $\sim 200 \mu\text{mol kg}^{-1}$ at 60° N in the northern part of the Atlantic and Pacific Oceans, with an average value of 182 $\mu\text{mol kg}^{-1}$ in the Southern Ocean, which is large enough to account by itself for most - but not all - of the nDIC latitudinal gradient of 223 $\mu\text{mol kg}^{-1}$ (2193-1970 $\mu\text{mol kg}^{-1}$).

The estimated overall uncertainty of SST-driven effect on surface nDIC (Table 2) ranges from 5 to 8 $\mu\text{mol kg}^{-1}$, which is of comparable magnitude to the uncertainty of DIC normalized to 2005, and much smaller than the large latitudinal variations of $\Delta\text{nDIC}_{\text{temp}}$.

3.3. Upwelling-driven effect in the Southern Ocean

5 The upwelling-driven effects in the Southern Ocean calculated from both short- and long-term perspectives are shown in Fig. 8.

$\Delta\text{nDIC}_{\text{upw_st}}$ increases polewards (Fig. 8a-c), with the same trends as surface phosphate (not shown), because it is calculated from phosphate. It can be seen that surface nDIC is potentially elevated dramatically by the Southern Ocean upwelling (~~up to about 250 $\mu\text{mol kg}^{-1}$~~). The effect is of larger magnitude (average of ~~208-220 $\mu\text{mol kg}^{-1}$~~ in the Southern Ocean) than that
10 calculated for $\Delta\text{nDIC}_{\text{temp}}$ (Fig. 7g-i).

Fig. 8d-f show the long-term effect of upwelling, which are controlled by the concentration of TA in the upwelled water (how much upwelling increases surface TA values by). The average magnitude of $\Delta\text{nDIC}_{\text{upw_lt}}$ is around 74 $\mu\text{mol kg}^{-1}$ for the Southern Ocean.

The estimated overall uncertainty of upwelling-driven effects on surface nDIC (Table 2) ranges from 5 to 9 $\mu\text{mol kg}^{-1}$, close
15 to the uncertainty of DIC normalized to 2005, and much smaller than the large latitudinal variations of $\Delta\text{nDIC}_{\text{upw_st}}$ and $\Delta\text{nDIC}_{\text{upw_lt}}$.

3.4. Iron-driven effect in the global surface ocean

As shown in Fig. 9, $\Delta\text{DIC}_{\text{Fe}}$ is close to zero except in the classic HNLC regions (i.e., the North Pacific, the equatorial Pacific, and the Southern Ocean, Moore et al., 2013). There is also some residual nitrate during most summers in the Iceland and
20 Irminger Basins of the North Atlantic due to the seasonal iron limitation there (Nielsdóttir et al., 2009). The surface Southern Ocean south of 40° S has the largest unused DIC ($\Delta\text{DIC}_{\text{Fe}}$ of up to ~~+65-180 $\mu\text{mol kg}^{-1}$~~ , average of ~~95-120 $\mu\text{mol kg}^{-1}$~~), followed by the North Pacific 40° N-65° N ($\Delta\text{DIC}_{\text{Fe}}$ of up to ~~90-120 $\mu\text{mol kg}^{-1}$~~ , average of ~~30-75 $\mu\text{mol kg}^{-1}$~~) and the equatorial Pacific (average of ~~+8-35 $\mu\text{mol kg}^{-1}$~~). It is negligible elsewhere in the tropics and subtropics.

4. Discussion

25 4.1. Factors controlling the surface DIC latitudinal variation

~~As shown in Fig. 7d-f, nDIC is about 223 $\mu\text{mol kg}^{-1}$ higher in the Southern Ocean, and about 192 $\mu\text{mol kg}^{-1}$ higher in the North Pacific, than at low latitudes (Table 4). Smaller increases of DIC are calculated, of about 150 $\mu\text{mol kg}^{-1}$ in the Southern Ocean, 50 $\mu\text{mol kg}^{-1}$ in the North Pacific and 100 $\mu\text{mol kg}^{-1}$ in the North Atlantic (Fig. 7a-c). Both DIC and nDIC are clearly higher, on average, at high latitudes. Fig 7d-f also show nDIC residuals after the estimated temperature effect is removed ($\text{nDIC}_{\text{SST}=27}$),
30 of around 50 $\mu\text{mol kg}^{-1}$ polewards in all basins in the southern hemisphere and of around 60 $\mu\text{mol kg}^{-1}$ (even higher) in the~~

~~North Pacific. The next few sections consider the contributions of different individual processes to the elevation of DIC and nDIC at high latitudes. The observed gradients are not solely due to temperature.~~

4.1.1. Effect of SST variation in the global surface ocean

The previously accepted explanation for higher DIC at high latitudes is that cooler SSTs there increase CO₂ solubility, resulting in a higher equilibrium DIC (Toggweiler et al., 2003a; Williams and Follows, 2011). Our results support an important role for SST, but also that other processes contribute significantly.

Our analysis concludes that the latitudinal gradient in temperature is capable of raising nDIC by about 180 $\mu\text{mol kg}^{-1}$ in the Southern Ocean, or in other words of explaining about four-fifths of the observed gradient of 223 $\mu\text{mol kg}^{-1}$. SST variation is thus able to explain most of the observed pattern.

10 4.1.2. Effect of TA distribution in the global surface ocean

A second factor that has been proposed as influential in driving spatial variations in the concentration of DIC in the surface ocean is TA (Williams and Follows, 2011). Our analysis supports this contention, although we note that the effect of TA is most prominent at low latitudes. Large differences in DIC are observed between the subtropical gyres, where values are relatively high, and the vicinity of the equator, where values are relatively low (Fig. 1a). These differences are driven by the effects of evaporation and precipitation on TA, which then drive differences in DIC because of the influence of TA on DIC at gas exchange equilibrium with a given atmospheric CO₂ level. The role of TA explains the much clearer relationship between latitude and nDIC than between latitude and DIC (Fig. 1, Table 3); normalizing DIC to salinity is almost the same as normalizing DIC to TA, because salinity and TA are highly correlated in the surface ocean. As a result, the effect of TA on DIC is counteracted by salinity normalization, with the pattern in nDIC (Fig. 1b) then revealing more clearly how other factors impact DIC.

The latitudinal pattern in TA is not the dominant driver of the DIC trend, because TA values are generally lower at high latitudes (where precipitation often exceeds evaporation) than they are at low latitudes (where evaporation often exceeds precipitation). However, TA is also biologically cycled and thus not perfectly correlated to salinity (Fry et al., 2015) and the presence of excess TA in deep water upwelled at high latitudes does contribute to the DIC trend.

25 4.1.3. Effect of upwelling in the Southern Ocean

Although not traditionally considered as a factor, our analyses show that upwelling is important in driving the latitudinal gradient in DIC. Upwelling of DIC by itself is capable of producing an nDIC latitudinal gradient of ~~208-220~~ $\mu\text{mol kg}^{-1}$ in the Southern Ocean, even higher than the effect of temperature (Fig. 8a-c, Table 4). However, the contribution of upwelling is reduced by about two thirds if only the long-term effect through upwelled TA is considered (see Fig. 6 for definitions of terms). Deep water usually has higher concentrations of nutrients, DIC and nTA than does surface water. Introduction of deep water into the surface mixed layer therefore usually stimulates increases in these concentrations, with three main consequences for

DIC (Fig. 6), as follows. (A) If the upwelled water has higher DIC than the surface then the upwelling causes an immediate initial increase in DIC; (B) additional nutrients stimulate phytoplankton blooms until the proximate limiting nutrient runs out, leading to a reduction in DIC over timescales of days to weeks (or months if, for instance, the upwelling occurs at high latitudes during winter when phytoplankton cannot bloom); (C) finally, air-sea gas exchange tends to remove any upwelling-induced air-sea CO₂ disequilibrium over a period of months to a year (Jones et al., 2014), although the full equilibrium is seldom achieved across the global surface ocean (Takahashi et al., 2014). ~~However, the amount of ingassing/outgassing potentially required to restore air-sea CO₂ equilibrium is a function of the amount of upwelled TA (which, together with temperature, controls the equilibrium DIC).~~

The upwelling effects in Fig. 8 are calculations based on phosphate and TA concentrations, taking into account both the amount upwelled, and the amount subsequently removed by biology. They therefore correspond to the sum of the direct upwelling effect (① in Fig. 6) and the indirect upwelling effect through supplied nutrients (② in Fig. 6). There are two reasons why the initial amount of upwelled DIC considerably exceeds the amount of DIC subsequently taken up by phytoplankton growth fueled by the upwelled nutrients (why ① > ②) in the Southern Ocean.

Firstly, iron is typically much scarcer in deep waters than are macronutrients, relative to phytoplankton need (Moore, 2016). Regions like the Southern Ocean that are strongly influenced by upwelling are for this reason often iron-limited (Moore, 2016), leading to large amounts of ‘unused DIC’ (order of 95-120 μmol kg⁻¹ in the Southern Ocean - Fig. 9) accompanying unused macronutrients. This scarcity of iron also leads to muted seasonal cycles of DIC (Merlivat et al., 2015) and thus year-round persistence of unused DIC. Secondly, as described in Sect. 2.4.5, the higher C:P ratio of supply (~109:1) compared to removal (~80:1) implies a considerable surplus of DIC even without iron limitation.

The upwelling effects shown in Fig. 8a-c are however relatively short-term, and are expected to be overridden by air-sea gas exchange within months (Jones et al., 2014). They are thus likely to be most significant in the vicinity of where upwelling takes place (Morrison et al., 2015). For effects that may persist further away from locations of upwelling, it is important to consider also the long-term effect (⑤ in Fig. 6), the magnitude of which is dictated mainly by the change in TA brought about by upwelling. The level of TA in upwelled water (~2315, 2340, and 2337 μmol kg⁻¹ in the Atlantic, Indian and Pacific sectors of Southern Ocean, respectively; calculated according to the same method as in Sect. 2.4.3) are higher than the typical levels of TA in the surface waters of the high latitude Southern Ocean (~2300, 2289, and 2288 μmol kg⁻¹ in the Atlantic, Indian and Pacific sectors, respectively). The increase in TA brought about by upwelling corresponds to a long-term upwelling effect on nDIC of about 74 μmol kg⁻¹ (Fig. 8d-f) in the Southern Ocean.

Our results show that upwelling in the Southern Ocean can, by itself, generate high-latitude nDIC values that are around ~~208~~ 220 μmol kg⁻¹ greater than subtropical values. We emphasize that there is, in addition, a sizeable long-term effect of upwelling (forcing nDIC values to be around 74 μmol kg⁻¹ higher than they would be otherwise). Contrary to what might typically be assumed, the long-term effects of upwelling are dictated by the amounts of TA upwelled, and not by the amounts of DIC or nutrients.

4.2. A new understanding of the controls on the surface DIC distribution

The analyses presented above show that our understanding of the causes of latitudinal gradient in DIC needs to be revised. Whereas it was considered previously that the latitudinal gradient in DIC is completely explained by sea surface temperature variation, here we have shown that upwelling is also an important contributor to it, based on an evaluation in the Southern Ocean. DIC and nDIC would still be elevated at high latitudes even if there was no temperature effect (even if CO₂ solubility was completely unaffected by SST). The incomplete previous view of what drives the DIC latitudinal gradients should be replaced by this more nuanced view in which upwelling is also seen to contribute.

It seems that neither temperature variation nor upwelling are responsible for all of the observed large latitudinal gradients in DIC and nDIC (for instance, the $\sim 223 \mu\text{mol kg}^{-1}$ difference in nDIC between low-latitudes and the Southern Ocean), but rather that they are jointly responsible. There is an apparent contradiction because both $\Delta\text{nDIC}_{\text{temp}}$ and $\Delta\text{nDIC}_{\text{upw_st}}$ appear to account for more than 80% of the nDIC latitudinal gradient. While both processes are capable individually of raising DIC by 182 and ~~208-220~~ $\mu\text{mol kg}^{-1}$ in the Southern Ocean, acting together they raise it by only $223 \mu\text{mol kg}^{-1}$ instead of ~~390-400~~ $\mu\text{mol kg}^{-1}$. An obvious explanation of this apparent paradox is that when we consider upwelling effects, we should consider not only its short-term effect through supplying DIC and nutrients ($\textcircled{1} + \textcircled{2}$ in Fig. 6), but also its long-term effect with gas exchange with the atmosphere ~~in the context of elevated TA by upwelling~~ ($\textcircled{5} = \textcircled{1} + \textcircled{2} + \textcircled{3}$ in Fig. 6). However, the amount of which ingassing/outgassing potentially required to restore air-sea CO₂ equilibrium is a function of the amount of upwelled TA (which, together with temperature, controls the equilibrium DIC). The sum of the SST-driven effect and the long-term effect of upwelling approximately equals the nDIC latitudinal gradient (Table 4).

On the global scale, therefore, the ultimate controls on the surface DIC and nDIC latitudinal gradients are the spatial patterns of SST and upwelling, and the chemical composition of the upwelled water.

4.3. Importance of upwelling confirmed by the North Atlantic

From inspection of the global nDIC distribution (Fig. 1b), it can be seen that nDIC increases with latitude in all basins, but, as shown in Table 4, does so less strongly in the North Atlantic (difference between high latitudes and low latitudes of $114 \mu\text{mol kg}^{-1}$) than in the North Pacific (difference of $192 \mu\text{mol kg}^{-1}$). Although the latitudinal temperature gradient is less pronounced in the North Atlantic, this is not enough to explain the variation in gradients between the two basins: the average temperature of the high-latitude North Atlantic is 12.4°C and of the high-latitude North Pacific is 9.5°C , which can explain about $20 \mu\text{mol kg}^{-1}$ of variation between the two nDIC gradients but cannot explain the observed $78 \mu\text{mol kg}^{-1}$ variation (Table 4).

The reason for the discrepancy is that the Southern Ocean and the North Pacific experience elevations in values due to inputs of deep water whereas the North Atlantic does not. Upwelling occurs in the Southern Ocean and entrainment due to deep winter mixing occurs in the subarctic North Pacific (Mecking et al., 2008; Ohno et al., 2009) where it entrains waters high in both TA (Fry et al., 2016) and DIC. While deep winter mixing also occurs in the high latitude North Atlantic (de Boyer Montégut et al., 2004), the entrained waters left the surface relatively recently and hence there is little accumulated

remineralized DIC and TA in the deep water that is reintroduced to the surface. For this reason, winter entrainment produces little increase in surface nDIC in the North Atlantic. This makes the North Atlantic useful in discriminating between the two effects because, uniquely out of the three regions, only the SST effect operates there. As expected, the SST effect is able to completely account for the observed nDIC gradient in the North Atlantic, whereas it cannot in the other two regions (columns 2 and 3 of Table 4). The North Atlantic confirms the important contribution of upwelling to latitudinal gradients, while also showing that latitudinal gradients occur in the absence of upwelling.

4.4. Comparison of nDIC distribution to Alk* and nutrients

Fig. 10 shows a comparison between the patterns of nDIC, the TA tracer Alk* (Eq. 11, Fry et al., 2015) and salinity-normalized nutrients. The similarities and differences in distributions of Alk* and nutrients have previously been discussed by Fry et al. (2015). Here we extend the comparison to also include nDIC. All exhibit low and fairly constant values at low latitudes, primarily due to biological uptake and restricted supply from subsurface waters, for most variables, but primarily due to fairly uniform high temperatures for nDIC. All increase polewards due to upwelling/entrainment (also SST for nDIC), exhibiting maxima at high latitudes in the Southern Ocean and North Pacific. All exhibit a more modest increase in the North Atlantic than in the North Pacific, because the deep water formed relatively recently. The coincident increases in nDIC and nitrate in the north Indian Ocean and equatorial Pacific Ocean are not matched by increases in either Alk* or silicate, most probably due to the source waters for the upwelling coming from depths that are shallower than the dissolution depths of calcium carbonate and opal (Fry et al., 2015; Schlitzer, 2000). There are differences in the latitudes at which the different parameters start to increase on a transect from the equator towards Antarctica, reflecting the different processes involved. Surface nDIC is the first to start increasing, under the influence of SST (rows 3 and 4 of Fig. 7), at around 20° S in the Atlantic and Pacific Oceans and 25° S in the Indian Ocean. Alk* and nitrate, on the other hand, do not start to increase until about 40° S in the Atlantic and Indian Oceans and about 30° S in the Pacific Ocean. Silicate does not increase in concentration until about 50° S, for reasons that are still debated (Assmy et al., 2013; Holzer et al., 2014; Vance et al., 2017).

4.5. Implications for the future CO₂ sink under climate change

It is widely understood that global warming may alter the spatial distribution and intensity of upwelling in the ocean (Bakun, 1990; McGregor et al., 2007; Wang et al., 2015). It could either increase it on average, due to higher average wind speeds in a warmer, more energetic atmosphere (Bakun, 1990; Wang et al., 2015), or decrease it on average, due to enhanced stratification as the temperature differential between surface and deep waters is increased (Barton et al., 2013; Sarmiento et al., 2004b). Furthermore, it is widely understood that an increase in upwelling would lead to an increase in the amount of CO₂ outgassed from the ocean, as larger quantities of CO₂-rich deep water are brought up to the surface and their CO₂ vented to the atmosphere (Evans et al., 2015; Marinov et al., 2006; Morrison et al., 2015). However, we have identified an additional effect here. Changes in upwelling would alter the distribution of carbon in the surface ocean not only through the supply of CO₂, but also through

the supply of TA which determines the eventual surface carbonate system equilibrium with the same atmospheric $p\text{CO}_2$ (Humphreys et al., 2018). That is to say, the impact of changes in upwelling on the ocean's carbon source/sink strength depends not only on the DIC content of the upwelled water but also on its TA content. Ocean carbon cycle models should include these additional consequences if they are to make accurate predictions about the impacts of global warming on future carbon cycling.

5 They should include the several routes identified here by which upwelling affects surface DIC: through upwelling of DIC, through upwelling of nutrients, and through upwelling of TA.

5. Conclusions

We investigated the global surface DIC and nDIC distributions in order to explain the large differences between high latitude (especially Southern Ocean) and low-latitude regions. This issue has been addressed in previous studies and here we revisited

10 it using new analytical approaches that lead to new findings. We considered three drivers for how the phenomenon could be explained: (1) sea surface temperature variations through their effect on CO_2 system equilibrium constants, (2) salinity-related TA variations through their effect on $p\text{CO}_2$, and (3) upwelling in the subpolar oceans. Our analyses confirmed that temperature plays a dominant role through its effect on solubility, and is able to explain a large fraction of the surface nDIC latitudinal gradient ($182 \mu\text{mol kg}^{-1}$ out of $223 \mu\text{mol kg}^{-1}$ in the high-latitude Southern Ocean). Variations in TA associated with

15 evaporation and precipitation are unable to explain higher DIC concentrations at higher latitudes, because alone they would drive the opposite DIC pattern. Their role is therefore to reduce the magnitude of the polewards gradient in DIC. Upwelling, whose role in driving the large-scale spatial patterns has not previously been appreciated, accounts for a sizeable component of the surface nDIC latitudinal gradient (~~up to $250 \mu\text{mol kg}^{-1}$~~ , on average $208\text{--}220 \mu\text{mol kg}^{-1}$ in the Southern Ocean). Its importance is magnified by the iron limitation that frequently occurs in upwelling areas, leaving behind residual upwelled

20 excess DIC and macronutrients that cannot be utilized by biology. We emphasize that the upwelling of TA alongside DIC generates a prolonged effect that persists beyond CO_2 gas exchange re-equilibration timescales. The long-term effect of upwelling ($74 \mu\text{mol kg}^{-1}$ in the Southern Ocean) helps explain the shortfall between the observed nDIC latitudinal gradient ($223 \mu\text{mol kg}^{-1}$) and the magnitude of the temperature-driven effect ($182 \mu\text{mol kg}^{-1}$). On the global scale, we conclude that no single mechanism accounts for the full amplitude of surface DIC latitudinal variations but that temperature and the long-term

25 effect of upwelling, in that order, are the two major drivers.

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Table 1.

Definitions of Subscripts and Main Terms used in the Text. X represents any variable involved in the calculations. The program CO₂SYS was used to calculate values under different conditions.

<i>Subscript</i>	<i>Meaning</i>
<i>Referring to (n)DIC values at a particular location</i>	
X_{supply}	Value at depth, along isopycnals that upwell at this location
X_{surf}	Predicted value in the surface layer
X_{obs}	Observed value at this surface location
<i>Referring to predicted (n)DIC values under different conditions</i>	
$X_{\text{SST}=27}$	Predicted value with sea surface temperature changed to 27°C
X_{nonupw}	Predicted value with upwelled TA subtracted
<i>Referring to changes in (n)DIC values because of processes</i>	
ΔX_{Fe}	Effect of iron limitation (biological drawdown that is prevented)
ΔX_{temp}	Effect of sea surface temperature variations
$\Delta X_{\text{upw_st}}$	Short-term effect of upwelling, through upwelled DIC
$\Delta X_{\text{upw_lt}}$	Long-term effect of upwelling, through upwelled TA
<i>Carbonate variables used to calculate predicted DIC values with CO₂SYS</i>	
$\text{DIC}_{\text{SST}=27} = f(T_{\text{SST}=27}, S_{\text{in-situ}}, \text{TA}_{\text{in-situ}}, p\text{CO}_{2,\text{in-situ}})$	$\text{DIC}_{\text{SST}=27}$ is a function of in-situ S, TA, and $p\text{CO}_2$, and SST at 27°C
$\text{DIC}_{\text{nonupw}} = f(T_{\text{in-situ}}, S_{\text{in-situ}}, \text{TA}_{\text{nonupw}}, p\text{CO}_{2,\text{in-situ}})$	$\text{DIC}_{\text{nonupw}}$ is a function of in-situ SST, S, and $p\text{CO}_2$, and pre-upwelling TA

Table 2.**Uncertainties for variables in this study.**

<i>Initial Variable</i>	<i>Uncertainty</i>	<i>Reference</i>
Salinity	0.005	Olsen et al. (2016)
Phosphate	0.05 $\mu\text{mol kg}^{-1}$	Olsen et al. (2016)
DIC	4 $\mu\text{mol kg}^{-1}$	Olsen et al. (2016)
TA	6 $\mu\text{mol kg}^{-1}$	Olsen et al. (2016)
$p\text{CO}_2$	6.8 μatm	Takahashi et al. (2014)
DIC normalized to 2005	5.0 $\mu\text{mol kg}^{-1}$	derived in this study ^a
Alk*	6.1 $\mu\text{mol kg}^{-1}$	Modified from Fry et al. (2015)
nPhos _{supply} , Alk* _{supply} , nDIC _{supply}	See text in Sect. 2.4.3	derived in this study ^b
<i>Calculated Propagated Uncertainties</i>		
$\Delta\text{nDIC}_{\text{temp}}$	8.0 $\mu\text{mol kg}^{-1}$	derived in this study
$\Delta\text{nDIC}_{\text{upw_st}}$	5.4 $\mu\text{mol kg}^{-1}$	derived in this study
$\Delta\text{nDIC}_{\text{upw_lt}}$	8.9 $\mu\text{mol kg}^{-1}$	derived in this study

^athe uncertainty of DIC normalized to 2005 was primarily propagated from TA and $p\text{CO}_{2,\text{sw}}^{2005}$. The uncertainty of $p\text{CO}_{2,\text{sw}}^{2005}$ was calculated from error propagation (Fornasini, 2008), to be 0.17 μatm .

5 ^bthe uncertainties for variables with subscript “supply” were from their standard error of the mean.

Table 3.**Global and Regional Correlations Between DIC, nDIC and SST, Latitude.**

Ocean	Region	DIC vs. Lat		nDIC vs. Lat		DIC vs. SST		nDIC vs. SST	
		ρ^a	N ^b	ρ	N	ρ	N	ρ	N
Global		0.71	14228	0.86	14228	-0.78	14228	-0.94	14228
Southern Ocean	S of 40° S	0.79	3061	0.81	3061	-0.93	3061	-0.95	3061
North Atlantic	N of 40° N	0.30	1640	0.58	1640	-0.34	1640	-0.78	1640
North Pacific	N of 40° N	0.02	1601	0.34	1601	-0.78	1601	-0.87	1601

^athe Spearman's rank correlation coefficient, for assessing monotonic relationships (there is a non-linear relationship between SST and CO₂ solubility). Statistically significant correlations are shown in bold.

5 ^bThe number of data points from that area that were used in calculating the correlations.

Table 4.

Summary of nDIC Differences Between Low and High Latitudes. Each Δ nDIC value is the amount by which the average nDIC value for the high latitude region exceeds the average value for the low latitudes (30° S to 30° N). %'s in brackets represent the ratio to the observed nDIC difference in column 2. n.c. = not calculated.

Region ^a	Observed Δ nDIC ($\mu\text{mol kg}^{-1}$)	Δ nDIC _{temp} ($\mu\text{mol kg}^{-1}$)	Δ nDIC _{upw_st} ($\mu\text{mol kg}^{-1}$)	Δ nDIC _{upw_lt} ($\mu\text{mol kg}^{-1}$)
Southern Ocean	223	182 (82%)	208-220 (93-98%)	74 (33%)
North Atlantic	114	122 (107%)	n.c.	n.c.
North Pacific	192	137 (71%)	n.c.	n.c.

5 ^aThe regions are defined as follows: North Atlantic: 40° N - 60° N; North Pacific: 40° N - 60° N; Southern Ocean: S of 40° S.

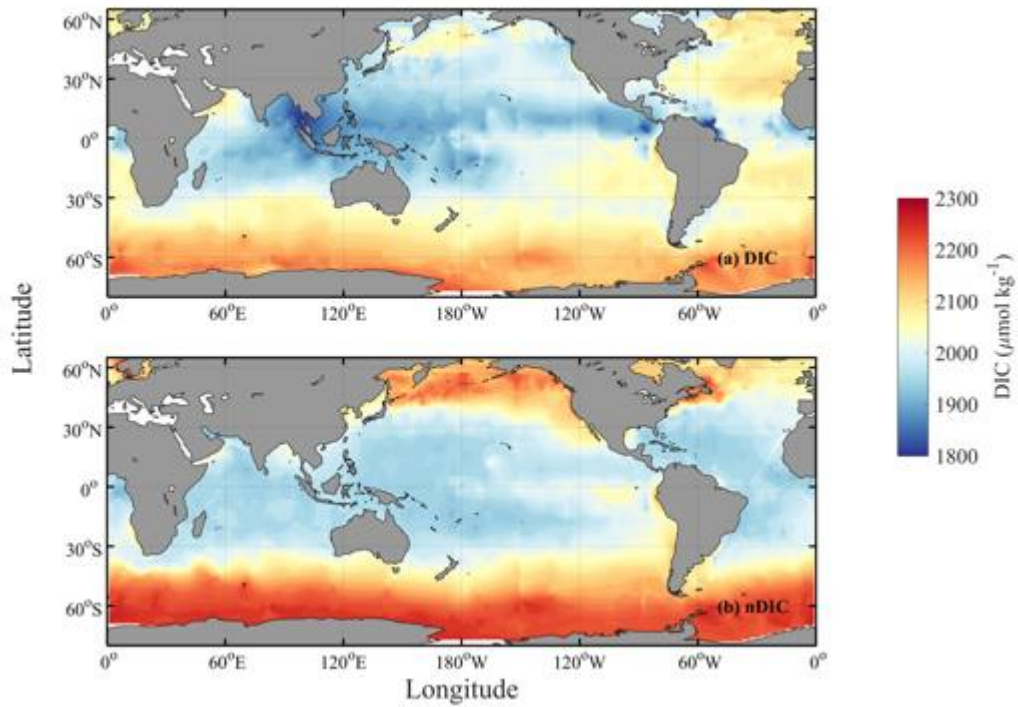


Figure 1. Spatial distributions of DIC and nDIC. (a) DIC (normalized to year 2005), (b) salinity-normalized DIC (nDIC, DIC normalized to reference year of 2005 and salinity of 35) in the surface global ocean. The latitudinal trends are clear, particularly for nDIC.

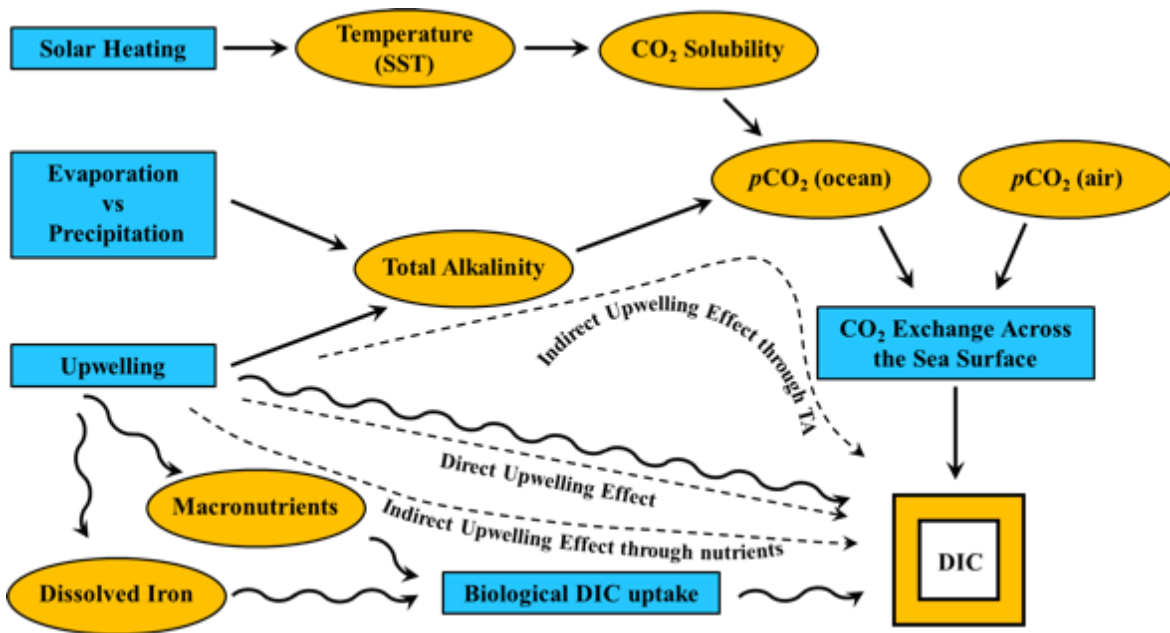


Figure 2. Major controls on surface DIC. Schematic showing the main processes exerting an influence over the concentration of DIC in the global surface ocean (producing variation with latitude). Blue shapes are processes and orange shapes are variables. Straight solid arrows represent equilibrium processes regulating nDIC in the long-term and wavy solid arrows represent disequilibrium processes regulating nDIC in the short-term. In the manuscript, we evaluate the upwelling effect on surface DIC in the Southern Ocean. Dashed arrows with text denote the three different ways that upwelling affects DIC: the direct effect through upwelled DIC; the indirect effect through upwelled nutrients which stimulates biological removal of DIC; and the indirect effect through upwelled TA in changing the equilibrium DIC with the atmosphere.

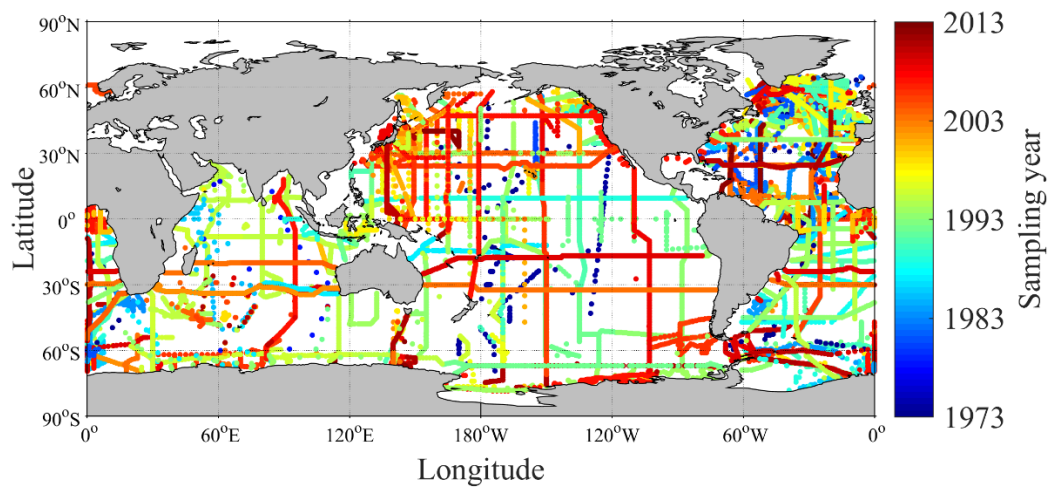


Figure 3. Spatial and temporal distribution of GLODAPv2 sampling stations used for this study.

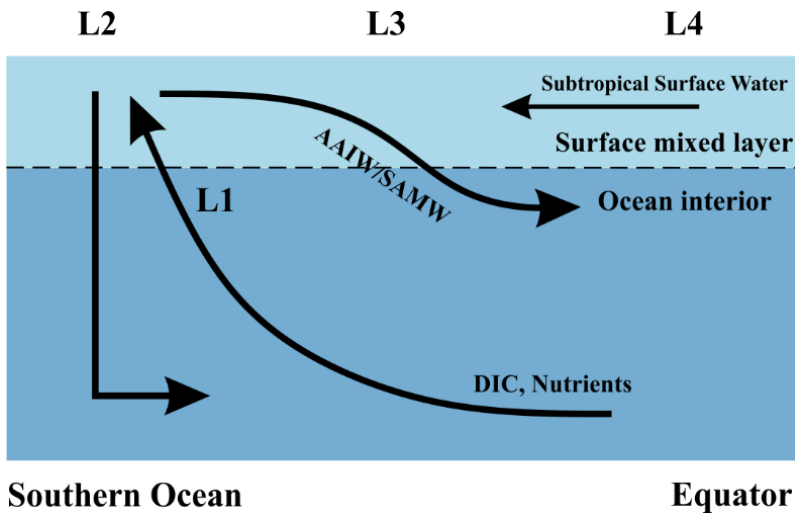


Figure 4. A schematic illustrating locations of interest and assumed major flow paths in the Southern Ocean. Black arrows represent the flow directions of water masses. The lower curved arrow denotes upwelling of deep water along isopycnal surfaces, and the upper curved arrow denotes subduction to form Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW). L1: upwelling water below the mixed layer, prior to any influence of surface processes; L2: sea surface within the core of the Southern Ocean upwelling south of 50° S (Morrison et al., 2015); L3: sea surface from 30° S to 50° S; L4: sea surface north of 30° S which experiences no direct effects from upwelling in the Southern Ocean.

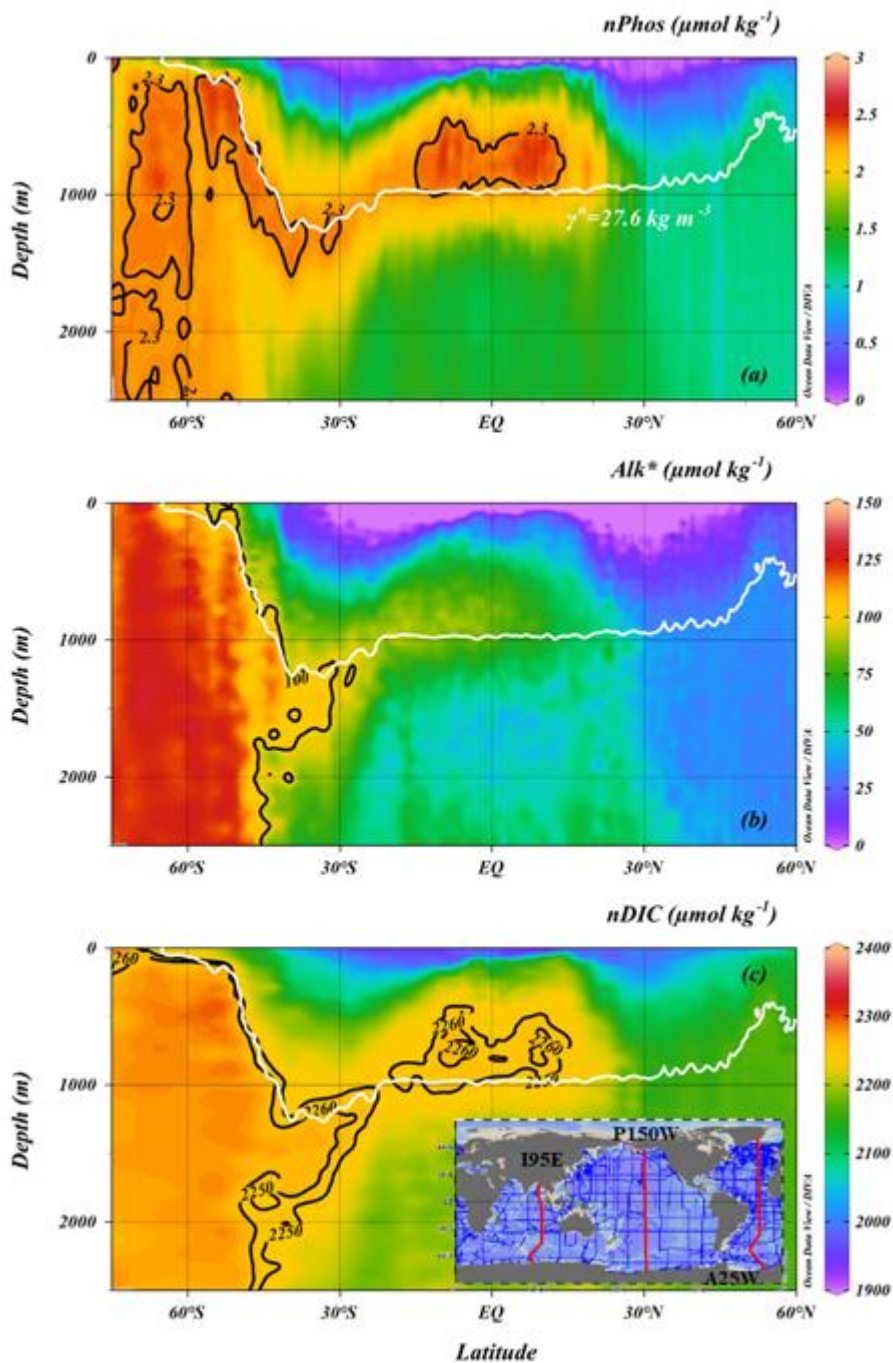


Figure 5. Vertical distributions of (a) nPhos, (b) Alk* and (c) nDIC along the Atlantic Ocean section. The Indian and Pacific sections are not shown. The selected Atlantic section (A25W) is shown as the red line on the right-hand side of the inset. The neutral density isopycnal along which upwelling occurs is indicated by the white contour, with the black contours referring to the observed variable.

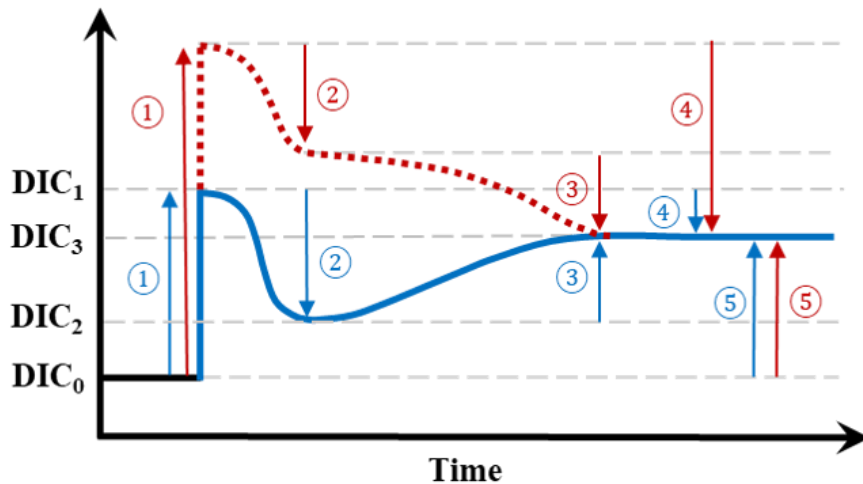


Figure 6. A schematic illustrating the various effects of upwelling on surface DIC. Numbers represent processes changing surface DIC, arrows point in the direction of change: ①: the *direct effect* of upwelling which elevates surface DIC from DIC_0 to DIC_1 ; ②: the DIC uptake by biology supported by upwelled nutrients, dropping DIC from DIC_1 to DIC_2 . The processes of ① and ② make up the *short-term* effect of upwelling (i.e., difference between DIC_2 and DIC_0); ③: the change brought about by air-sea CO_2 gas exchange which continues towards the equilibrium with the atmosphere (DIC_3 , whose level is determined by the amount of upwelled TA as well as by temperature); ④: the combination of both ② and ③ makes up the total *indirect effect* of upwelling (the difference between DIC_3 and DIC_1); ⑤: the *long-term* impact of upwelling on the level of surface DIC is the difference between DIC_3 and DIC_0 . Blue and red indicate two scenarios with different amounts of upwelled DIC relative to upwelled TA, but the same amounts of upwelled TA. Blue is for upwelled water with a deficit in additional DIC relative to additional TA whereas red is for an excess in DIC relative to TA.

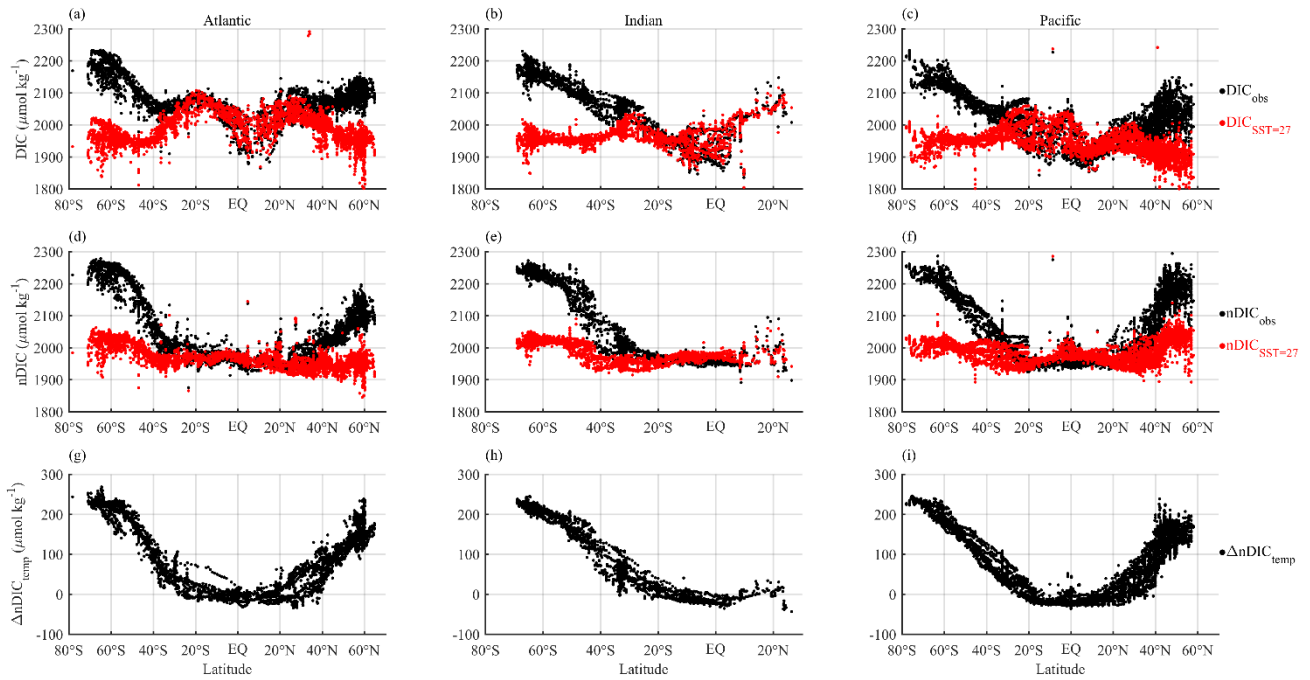


Figure 7. Latitudinal distributions of calculated temperature effect on surface DIC. Different columns show different basins (Atlantic, Indian and Pacific) and different rows show different calculated DIC variables. a, b and c show the observed surface DIC (black) and predicted DIC at SST of 27°C (red). d, e and f show the observed surface nDIC (black) and predicted nDIC at SST of 27°C (red). g, h and i show $\Delta n\text{DIC}_{\text{temp}}$, where $n\text{DIC}_{\text{SST}=27}$ is subtracted from $n\text{DIC}_{\text{obs}}$ to obtain the calculated temperature effect.

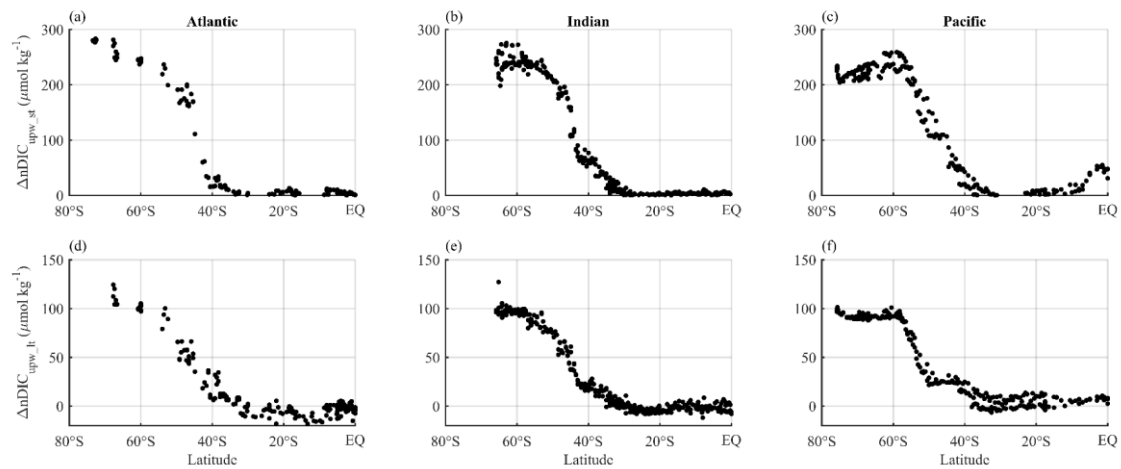
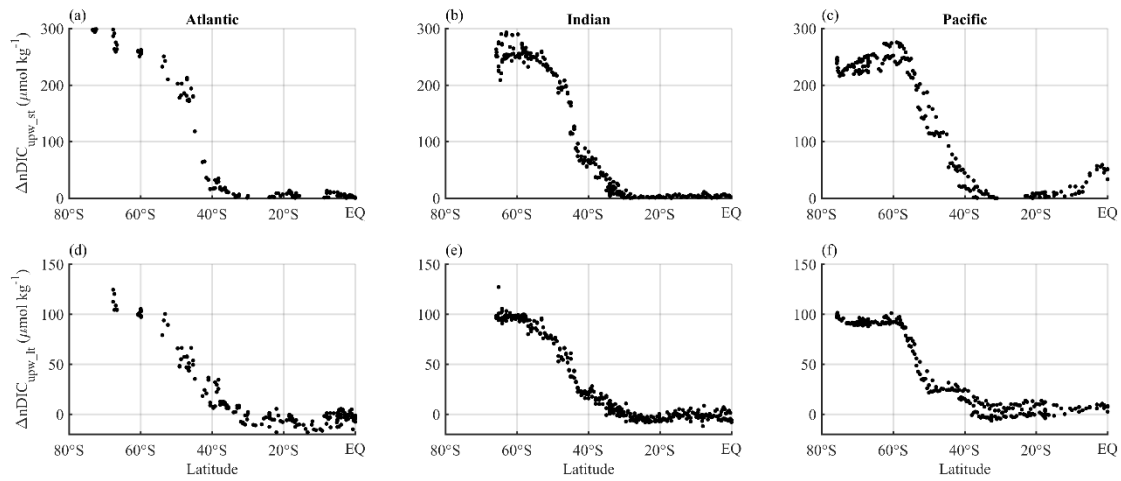


Figure 8. Latitudinal distributions of calculated upwelling effects on surface nDIC. Different columns show different sectors in ocean basins (Atlantic, Indian and Pacific) and different rows show different calculated effects on surface DIC. a, b and c show the short-term effect of upwelling ($\Delta n\text{DIC}_{\text{upw_st}}$), which is driven by the direct supply of DIC from deep water and subsequent change by biology in the Southern Ocean. d, e and f show the long-term effect of upwelling ($\Delta n\text{DIC}_{\text{upw_lt}}$), which is the difference between the observed nDIC value (determined mainly by the amount of upwelled TA, as well as by SST) and pre-upwelling nDIC value.

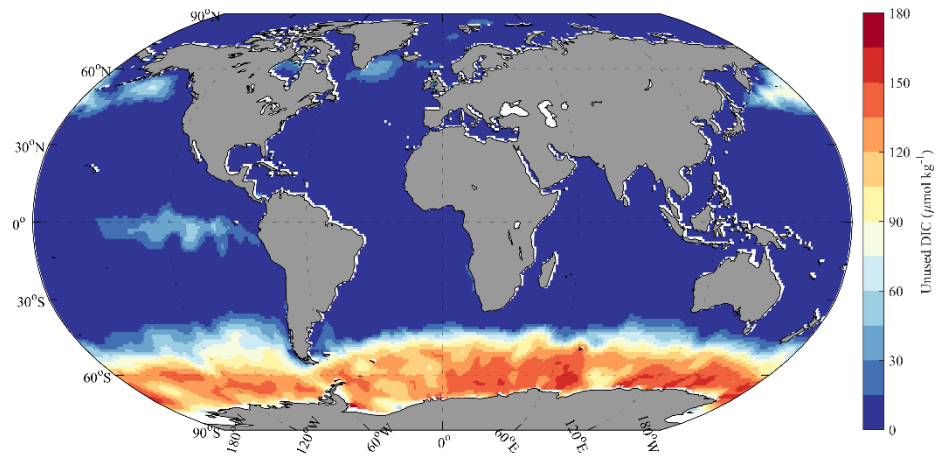
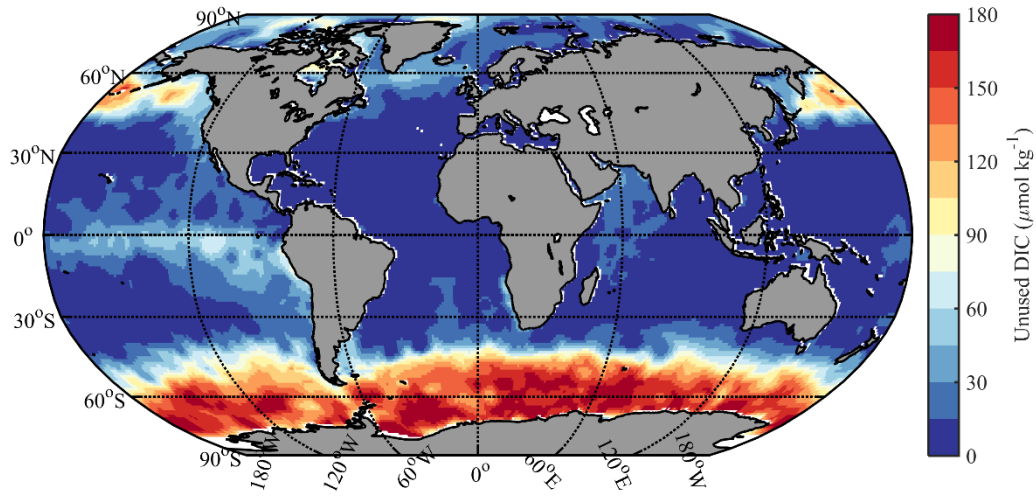


Figure 9. Calculated potential impact of iron limitation on surface DIC. Different colors correspond to different amounts of “unused DIC”, calculated by Redfield ratio from observed residual nitratephosphate.

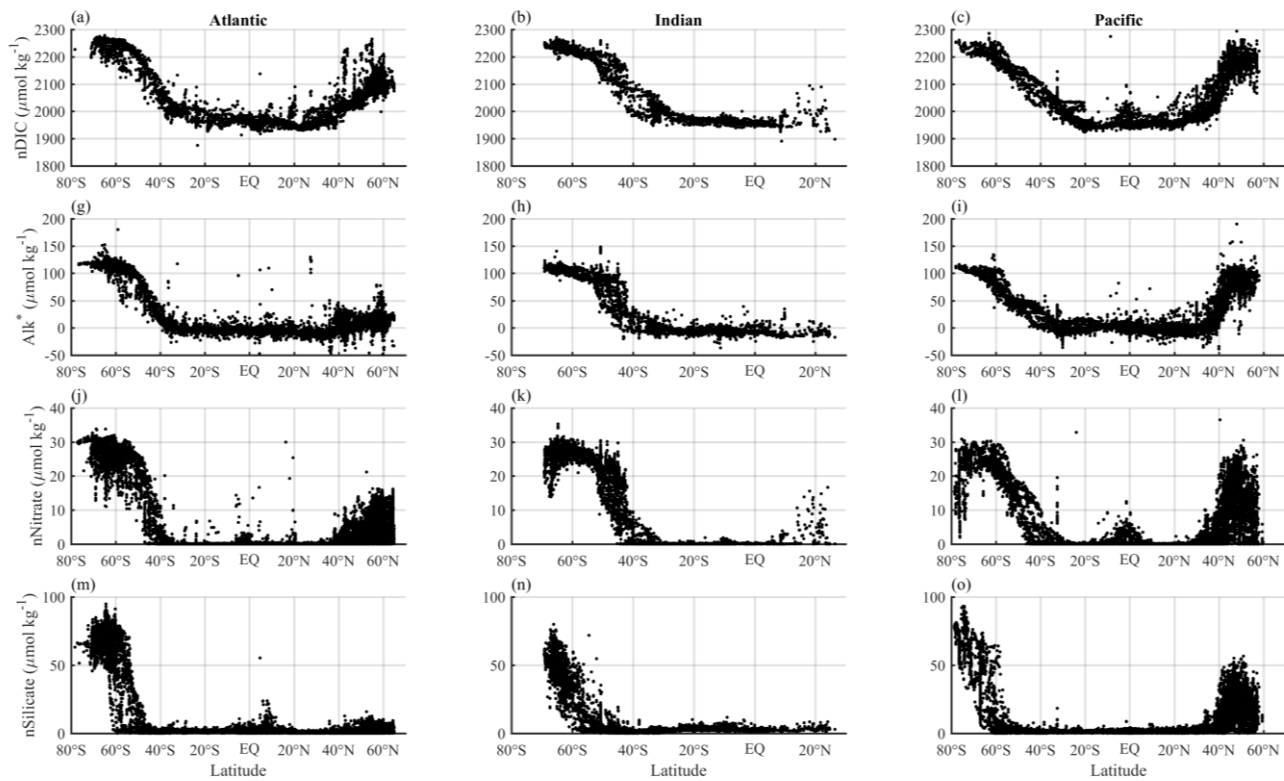


Figure 10. Latitudinal distributions of sea surface nDIC, Alk* (*Fry et al., 2015*), salinity-normalized nitrate and silicate in each ocean basin.