Impacts of climate change on air-sea exchanges of CO_2

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EXECUTIVE SUMMARY

The oceans are a significant sink for anthropogenic carbon dioxide (CO_2), taking up 2.3±0.5 petagrammes of carbon per year from the atmosphere (about one quarter of anthropogenic emissions) as CO_2 naturally dissolves in the water.

This net air-to-sea anthropogenic flux is in addition to an approximately globally-balanced natural cycle of CO_2 between the atmosphere and ocean.

Some of the in-gassed anthropogenic CO_2 remains in the surface ocean, increasing the partial pressure there, while the rest is mixed or carried into the deep ocean.

The ocean uptake of CO_2 is expected to decrease during the 21st Century due to a number of factors:

  a. the additional CO_2 will increase the proportion present as dissolved gas rather than as bicarbonate and carbonate ions;

  b. rising sea-surface temperatures will reduce the solubility of CO_2 in sea-water;

  c. slowing ocean circulation will reduce the transport to depth;

  d. reduction in biological activity may reduce the sinking flux of particulate organic carbon.

Reductions in the uptake flux have been seen in recent decades in two regions with large net air-to-sea fluxes of anthropogenic CO_2 (the North Atlantic and the Southern Ocean) but it is not clear if these are long-term trends or short-term variability.

The continental shelves are very important in the natural carbon cycle, but it is not clear what role they will play in the future uptake of anthropogenic CO_2.

Increased monitoring, using automated sensors on moored buoys, drifting floats and commercial shipping, is essential to better understand the ocean uptake of anthropogenic CO_2.

1. WHAT IS ALREADY HAPPENING?

Introduction

The ocean plays a significant role in the global carbon cycle, both the natural cycle and the anthropogenic perturbation over the last two centuries. The ocean contains around 38,000 petagrammes of carbon (PgC; 10^{15}gC) as dissolved inorganic carbon (DIC); this is almost 50 times the mass of carbon present as CO_2 in the atmosphere currently (2013) and more than 60 times the pre-industrial atmospheric inventory. (Note that here the mass of carbon in the carbon dioxide, not the mass of carbon dioxide itself, is measured; the corresponding mass of CO_2 is 3.67 times as great.)

The surface waters of the ocean are continually exchanging CO_2 with the over-lying atmosphere. The size of the flux, and in particular whether it is from the atmosphere into the ocean (air-to-sea) or vice-versa, varies geographically and on time-scales of days, to seasons, to years. In pre-industrial times the amount of carbon dissolved in the global ocean was approximately constant: the estimated net flux of around 0.6 PgC/yr from the ocean to the atmosphere was balanced by a similar flux of carbon delivered to the ocean by rivers. However, anthropogenic releases of CO_2 to the atmosphere during the industrial era have caused a net flux from the atmosphere to the ocean of 2.5±0.5 PgC/yr (calculated from the submissions of four ocean carbon-cycle models to the Global Carbon Project carbon budget, averaged over the 10 years 2002-2011, and with the uncertainty reflecting both the uncertainty in the mean ocean sink and the interannual variability in the model simulations; Le Quéré *et al.*, 2012). The ocean is therefore a net sink for anthropogenic CO_2, reducing the increase of CO_2 in the atmosphere and the climatic consequences.

How carbon dioxide is taken up by the ocean

Carbon dioxide, like many gases, dissolves naturally in water. The amount of CO_2 that can be dissolved in a certain amount of water depends on the salinity and the temperature: cold water can hold more dissolved gas than warm.

However, unlike most other gases, once in solution it reacts with the water to form bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}). The total inventory of dissolved inorganic carbon (DIC) is therefore the sum of the carbonate ion, bicarbonate ion and (unreacted) dissolved gas fractions. How much is found in each form depends on the temperature of the water and the concentrations of other chemical species dissolved in the water. In typical seawater at the surface of the ocean today out of every 100 molecules or ions contributing to DIC approximately 93 will be bicarbonate ions, 6 will be carbonate ions and only 1 will be in the un-reacted dissolved gas form. Although individual molecules and ions are continually changing from one form to another through reactions the proportions remain constant overall. The greatly increased capacity for CO_2 uptake by the ocean as a result of these chemical reactions is referred to as the buffer capacity of sea water, and it is expected to decrease as more CO_2 dissolves in the ocean.

The rate of transfer of CO_2 between the atmosphere and the surface ocean is governed by the difference in the partial pressures (ΔpCO_2) in the atmosphere and ocean, the solubility of CO_2 and by physical factors such as wind-speed and ocean temperature (which are expressed in the transfer velocity). Since the atmosphere is relatively well-mixed its partial pressure of CO_2 shows little geographical variation at any given time and little variation over the course of a year (the amplitude of the seasonal cycle at Point Barrow in Alaska, for example, is around 15 micro-atmospheres (μatm) compared to a mean value in 2011 of 390 μatm). In contrast, that of the surface ocean shows an annual mean geographical range of over 100 μatm, and individual locations can show seasonal variations of 60 μatm or more (LDEO database, 2013; Takahashi and Sutherland, 2013). The geographical variation is mainly caused by the ocean circulation: high-latitude regions where the water is cold and dense, and where water sinks to the deep ocean, have a low pCO_2 and are net sinks for atmospheric CO_2, while low-latitude regions, especially those like the Equatorial Pacific where deep DIC-rich water upwells to the surface, have high pCO_2 and out-gas CO_2 to the atmosphere. The seasonal variation is due to several factors, with different ones dominating at different locations: in some places, particularly at mid- and high-latitudes, intense seasonal biological activity causes a sharp reduction in DIC (due to the carbon being taken up by phytoplankton for photosynthesis and growth) which means the pCO_2 decreases in the summer. In other regions, where biological activity is less significant, the higher temperatures in summer mean a lower solubility and so the relatively-constant DIC concentration has a higher pCO_2 at that time; while in still others deep convection events at certain times of the year can mix up high-CO_2 waters to the surface where they warm and out-gas.

The transfer velocity is strongly dependent on the wind just above the surface ocean, increasing as the square or the cube of the wind-speed. A number of parameterisations are available, including those due to Liss and Merlivat (1986), Wanninkhof (1992) and Nightingale *et al.* (2000); of those, that due to Wanninkhof (1992) is most commonly used. It is recognised that the sea state, i.e. the height and steepness of the waves, is also important, but the effects are less well quantified and no parameterisations of sea-state are currently used in ocean carbon cycle models.

Physical and biological processes within the ocean are important for re-distributing the CO_2 that has entered the surface waters from the atmosphere. The deep ocean has a higher DIC concentration than the surface ocean, and this concentration gradient is maintained by the action of two 'pumps': the biological pump and the solubility pump. The biological pump is the uptake of DIC in the sun-lit surface waters by phytoplankton for photosynthesis and growth, some of which is not returned to solution until the phytoplankton have died (often by being eaten by zooplankton) and the remains of their cells have sunk into the deep ocean (against the concentration gradient). The solubility pump is due to the fact that the areas where the temperature of the surface ocean is low, are both those where the pCO_2 is low and so the in-gassing of CO_2 is high (due to high solubility) and also where deep water forms (the cold dense water sinks readily away from the surface, taking its dissolved gases with it). Therefore the deep ocean is ventilated by high-DIC water from the surface rather than by surface water with an average DIC concentration. If these pumps did not operate the DIC concentration throughout the ocean would equalise, that in the surface water would rise and so the atmospheric CO_2 concentration would increase also.

The fluxes

It is estimated (Prentice *et al.*, 2001) that approximately 90 PgC in the form of CO_2 entered the ocean each year in the pre-industrial carbon cycle, balanced by a similar-sized flux out of the ocean; therefore the net flux (averaged over several years) was just the 0.6 PgC/yr out-gassing of river-supplied carbon previously mentioned. However, perturbations to the carbon cycle have been caused during the last 250 years by human activities: mainly the burning of fossil fuels and the clearance of forests. Le Quéré *et al.* (2012) calculate that during the decade 2002 to 2011 the average emissions were 8.3±0.4 PgC/yr from fossil fuels and cement manufacture and 1.0±0.5 PgC/yr from land use changes and over that period the annual fossil fuel emissions increased by 3.1%/yr.

The net flux into the ocean during the decade 2002-2011 is estimated to be 2.5±0.5 PgC/yr (Le Quéré *et al.*, 2012). Therefore the ocean is currently taking up just over 25% of the total anthropogenic emissions. This net flux is mainly due to the additional, anthropogenic, CO_2 in the atmosphere, but also contains minor contributions due to the effects of climate change on the natural (pre-industrial) carbon cycle and the effects of climate change on the anthropogenic CO_2 flux (these minor contributions may oppose the anthropogenic flux). It is not practical to separate these contributions in

observations, though it is possible in model simulations. As the additional CO_2 enters the ocean it increases the DIC content and so also the ocean surface pCO_2; because the atmospheric pCO_2 is continually being increased by anthropogenic emissions the ocean pCO_2 will continue to rise also. Khatiwala *et al.* (2009) estimate that up to 2008, a total of 140±25 PgC of anthropogenic carbon had been stored in the ocean since the start of the industrial era (plus perhaps another 11 PgC in the Arctic, which was outside the area of their main calculation).

Model simulations are also required to identify the geographical regions where the flux of anthropogenic CO_2 into the ocean is strongest. Models consistently show that the polar and sub-polar North Atlantic and areas of the Southern Ocean are the main areas where anthropogenic CO_2 enters the ocean. These areas are, not coincidentally, those where deep water formation occurs: the sinking water carries the newly in-gassed anthropogenic CO_2 away from the surface and allows more to be taken up by the ocean.

Continental shelves play an important role in the natural carbon cycle, with dissolved and particulate organic matter being received from the terrestrial biosphere via rivers, biological growth and respiration in the shelf waters themselves, and the export of DIC and dissolved and particulate organic carbon to the deep waters of the adjacent ocean. The spatial and temporal heterogeneity of the shelf environments makes estimating the fluxes and stores of carbon there very difficult, but a number of estimates have been attempted both globally and for particular shelf regions including the North-West European Shelf. Chen and Borges (2009) estimate that, globally, shelf seas are net sinks for atmospheric CO_2 (but estuaries are net sources). Thomas *et al.* (2004) estimate, through observations and modelling, that the North-West European Shelf is a net sink, and exports 93% of the CO_2 taken up to the North Atlantic; Borges *et al.* (2005) also conclude that this shelf is a net sink. No estimates have been published that separately calculate the air-to-sea CO_2 flux in different areas of this shelf. Data are now being collected regularly by research groups from a number of countries using autonomous instruments installed in commercial ships (including ferries) that operate on the shelf but the data coverage is not yet adequate to fully characterise the flux and the funding for such activities is insecure.

2. WHAT COULD HAPPEN?

The main problem facing the assessment of future changes in ocean uptake of CO_2 is the short time-period over which observations have been available. No more than three decades of data are available globally, and for much of that time some regions (e.g. the Southern Ocean) were barely sampled at all. This means that it is often difficult to determine with confidence which observed changes over time are due to trends in climate or atmospheric CO_2 and which are due to natural climate cycles (e.g. El Niño/La Niña, North Atlantic Oscillation, Pacific Decadal Oscillation). Model simulations forced by observed weather reanalyses can help with this determination.

Le Quéré *et al.* (2010) used a model forced by NCEP reanalyses (NCEP 2001, updated) and found that the global decadal-average air-to-sea flux of anthropogenic CO_2 should have been rising at a rate of 0.32 PgC/yr per decade over the period 1981-2007, based on the rise in atmospheric pCO_2. However, they calculated that the effect of climate change over the same period was to reduce the sink by 0.20 PgC/yr per decade, so the actual rise was only 0.12 PgC/yr per decade, less than 40% of what it would have been without climate change.

Changes over time in the air-to-sea flux are mainly due to changes in the disequilibrium between atmospheric and ocean surface pCO_2 values. (One exception to this is in high-latitude regions where significant reductions in the area covered by ice can allow more of the ocean to in- or out-gas CO_2.) The atmospheric CO_2 content rose during the decade 2000-2009 at an average rate of 1.9 μatm/yr (converting from the mass-based rate of 4.0±0.2 PgC/yr in Conway and Tans, 2011); so if the ocean surface pCO_2 value rises more slowly than this the air-to-sea flux will increase, but if it rises faster the flux will decrease. There are a small number of time-series stations where both atmospheric and ocean pCO_2 values have been recorded for more than a decade, and the results are highly dependent on the location.

• At the Bermuda Atlantic Time-series Study site (BATS, 31°40'N, 64°10'W) from 1983 to 2005 Bates (2007) showed (with a linear fit) pCO_2^{atm} rising by 1.78 μatm/yr and pCO_2^{ocn} by 1.67 μatm/yr, while with seasonal detrending applied to the data both pCO_2^{atm} and pCO_2^{ocn} rose by 1.80 μatm/yr; in the first case the sink will have increased but it will have remained constant in the second.

• The Hawaii Ocean Time-series (HOT) at Station ALOHA (22°45'N, 158°00'W) between 1988 and 2007 showed (Dore *et al.*, 2009) pCO_2^{atm} rising by 1.68 μatm/yr but pCO_2^{ocn} rising by 1.88 μatm/yr, implying a decreasing sink.

• González-Dávila *et al.* (2010) reported that at the ESTOC site (29°10'N, 15°30'W; near the Canary Islands) from 1995 to 2004 pCO_2^{atm} rose by 1.6 μatm/yr while pCO_2^{ocn} rose by 1.55 μatm/yr: an increasing sink.

• However, between 1985 and 2006 at a monitoring station in the Iceland Sea (68.0°N, 12.67°W) Olafsson *et al.* (2009) reported pCO_2^{atm} rising by 1.69 μatm/yr but pCO_2^{ocn} rising by 2.15 μatm/yr, meaning a large decrease in the sink.

A number of recent studies (Schuster and Watson, 2007; Schuster *et al.*, 2009) have reported a reduction in CO_2 uptake in the North Atlantic between the mid 1990s and 2005 based on a number of repeat surveys (latterly made using automatic instrument packages on commercial ships crossing the Atlantic). Omar and Olsen (2006) and Corbière *et al.* (2007) also reported weakening of the North Atlantic sink over this period. Schuster and Watson (2007) suggested a link to changing ocean circulation patterns, while Corbière *et al.* (2007) suggested that rising sea-surface temperatures had the major influence, Metzl *et al.* (2010) linked quickly-rising winter pCO_2 values to stronger convection (which mixes more DIC-rich water up to the surface) and several studies (e.g. Thomas *et al.*, 2007; Ullman *et al.*, 2009; McKinley *et al.*, 2011) have tried to interpret the changing uptake in terms of known climate cycles including the North

Atlantic Oscillation. The network of commercial ships with automated instrument packages measuring surface ocean pCO_2 in the North Atlantic has expanded rapidly during the last few years, mainly co-ordinated through the EU-funded projects CarboOcean (between 2005 and 2009 inclusive) and CarboChange (from 2011): see Watson *et al.* (2009) for a description of the network, which will allow future changes to the North Atlantic sink to be closely monitored.

Le Quéré *et al.* (2007) identified, on the basis of an atmospheric inversion analysis, a reduction in the net sink in the Southern Ocean in recent decades. A model simulation, driven by observed heat fluxes and winds indicated that the known intensification of the zonal winds over the Southern Ocean would have increased convection in the ocean and mixed more DIC-rich water to the surface, perturbing the natural cycle to produce a larger out-gassing and so a smaller net total flux into the ocean. Since that paper further modelling studies (e.g. Lenton *et al.*, 2009) have suggested that this mechanism may be at least partly countered by increased eddy activity in the ocean (which was not included in the original model simulations); however, whatever the exact mechanism causing it, the weakening of the Southern Ocean sink has been supported by in-situ studies (e.g. Metzl *et al.*, 2009), though such surveys are necessarily localised and it is not clear that they can be regarded as indicative of the whole Southern Ocean.

Coupled climate-carbon cycle models have, since Cox *et al.* (2000), been used to produce projections of future climate change and future carbon sources and sinks. The models, which include the atmosphere, ocean and biogeochemical components, are driven by a number of scenarios (projections) of future anthropogenic CO_2 emissions (including land-use changes). The model projections consistently indicate that, in scenarios where the CO_2 emissions continue to rise through the 21st century, the ocean sink will take up a smaller percentage of the annual emissions, leaving more in the atmosphere where it can cause climate warming. (It should be noted, however, that the absolute size of the sink continues to increase.) The models consistently attribute this relative weakening of the sink to four processes: reduced solubility of CO_2; a change in the carbon chemistry, in particular an increase in the proportion of DIC that is in dissolved gas form (and so a given DIC concentration will give a higher ocean pCO_2 and a given pCO_2 value will correspond to a lower DIC content); a change in the ocean circulation, particularly a decrease in the rate of formation of deep water; and a reduction in the sinking flux of particulate organic carbon produced by surface ocean ecosystems (i.e. a weakening of the biological pump; Bopp *et al.*, 2001). The mechanisms behind the changes in these processes are understood: the solubility decreases as sea-surface temperatures rise; the change in the chemical buffering is due to an increase in the concentration of hydrogen ions when CO_2 dissolves in water, which is the principal effect of ocean acidification; the slowing of deep water formation is due to increased stratification in the surface ocean, caused in turn by increased fresh-water input from melting ice and by increased sea-surface temperatures; and the weakening of the biological pump is mainly due to

reduced nutrient supply because increased stratification has inhibited vertical mixing and upwelling (in some areas of the ocean where nutrients are always abundant biological activity increases due to shallower mixing keeping phytoplankton in well-illuminated near-surface waters, but in most areas – and globally – the effect of nutrient reduction is dominant).

It is not known how the uptake of CO_2 in the waters of the North-West European Shelf around the British Isles will change during the 21st century. Changes in ocean chemistry will certainly be significant, and reduced solubility of CO_2 because of warming surface waters will also reduce the net uptake. Increased stratification may inhibit the exchange of shelf and open-ocean waters, which would reduce both the export of DIC and organic carbon off the shelf and the supply of nutrients onto the shelf; though there are also significant supply mechanisms for nutrient from land via rivers and from shallow sediments which will not be inhibited by increased stratification. In fact the strength of biological production on the shelf is likely to be significantly affected by other, non-climate, anthropogenic influences, including changes to nutrient loadings in rivers (due to changes in agricultural practices on land) and changes to grazing pressure (due to changing abundances of fish as a result of fishing policies). Models capable of representing all these factors and processes over long time-scales on the shelf are only just becoming available, building on existing successful models such as ERSEM (Blackford *et al.*, 2004).

3. KNOWLEDGE GAPS

a. More intensive monitoring (spatially and temporally) of the carbon system, and of ecosystem activity and nutrient flows, in the open ocean and in shelf waters. This will mean more automated sensors on buoys and on commercial shipping, and additional research cruises for process studies and sensor calibration. This would be best done as part of existing international projects such as the Global Ocean Observing System (GOOS) and the Integrated Carbon Observing System (ICOS).

b. More understanding of how physical processes (e.g. near-surface vertical mixing by ocean eddies) and biological organisms interact (on scales of a few kilometres) to produce the sinking flux of particulate organic carbon, and how that flux is respired and remineralised in the intermediate-depth and deep waters: this is the essential process of the biological pump.

c. More understanding of how the above processes will change with changing climate, and how they will feedback on the concentrations of greenhouse gasses in the atmosphere and so on climate change.

4. SOCIO-ECONOMIC IMPACTS

a. The projected weakening of the ocean sink for CO_2 will mean that more CO_2 will remain in the atmosphere and so the effects of climate change will be greater than otherwise. The likely social and economic consequences of that, in the United Kingdom and elsewhere, are still uncertain but UKCP09 (http://ukclimateprojections.defra.gov.uk) gives a range of possible outcomes for the UK and the 4th

Assessment Report of the IPCC (Parry *et al*., 2007) provides the most comprehensive description of the possible impacts across the world.

b. The main effect of the extra anthropogenic CO$_2$ entering the ocean is ocean acidification. As CO$_2$ dissolves in water it makes it more acidic (reduces its pH), and though no carbon cycle projections indicate that the ocean will become at all acidic (i.e. have a pH less than 7.0) during the 21st century (or even soon after) the changes that are projected (pH reduction from 8.1 to 7.8 or less) are expected to have significant impacts on marine organisms. The impacts fall into two categories: single-celled organisms (including ~~coral polyps and~~ some phytoplankton and zooplankton) that form shells of calcite or aragonite (both forms of calcium carbonate); and multi-celled organisms such as squid and fish (especially their larval stages). At present the calcium carbonate shells can be formed easily, and once formed have no tendency to dissolve again in the near-surface waters where the calcifying organisms live, but by the end of the current century the changing carbon chemistry (and in particular the change in the saturation state of calcite and aragonite) will mean that the energetic cost of shell-formation will be very high and will severely reduce the ability of those organisms to survive; and, once formed, the shells will easily dissolve again (Orr *et al*., 2005). In the case of fish, squid, etc., it is the reduction in the pH that affects their ability to regulate their internal body chemistry. There are many laboratory, mesocosm and modelling studies underway to quantify these effects, including a number funded as part of the Natural Environment Research Council's Ocean Acidification thematic plan. The socio-economic impacts arise because fish provide a major source of protein to human societies, and coral reefs are among the most productive ocean environments and provide a wide range of benefits to humans.

5. CONFIDENCE ASSESSMENT

What is already happening?
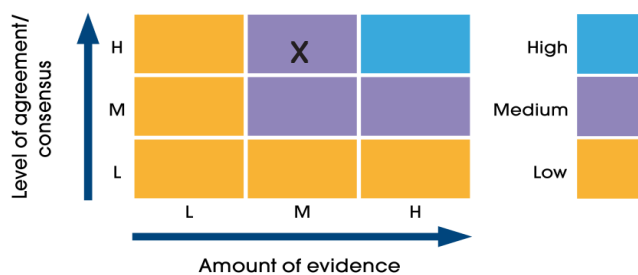
There is high confidence in the carbon chemistry, qualitatively and quantitatively.

There is high confidence in the physics of the uptake mechanism, and in the solubility quantitatively as a function of temperature, but there is uncertainty about the dependency of the transfer velocity on wind-speeds when those speeds are high.
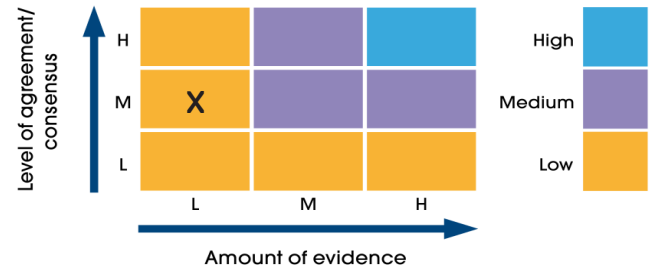
There is high confidence in the size of the emissions of CO$_2$ and of the change in the atmospheric content.

There is high confidence in the sign of the air-to-sea flux globally, and moderate confidence in its size globally and seasonally, but there is low confidence in the size of the fluxes regionally, and there is low confidence also in the size of the recent decadal variation globally.

There is moderate confidence that the shelf seas are a net sink for atmospheric CO$_2$ globally, but very low confidence in the size of the flux into the waters of the North-West European Shelf.

What could happen?

There is moderate confidence that the ocean sink will increase in strength in absolute terms but decrease as a proportion of emissions (if the rate of emissions continues to rise). There is moderate confidence in the size of the increase globally (for a specified emission scenarios).

There is low confidence in the size of the change in the ocean sink regionally (and even in the sign of the change in some regions).

There is moderate confidence in the sign of the changes in the sink in the North Atlantic and in the Southern Ocean seen over recent decades, but low confidence in the explanations.

In future scenarios there is high confidence in the predicted change in the carbon chemistry, but low confidence in the changes to the ocean circulation and low confidence in the changes in the strength of the biological pump (there is moderate confidence in the biological processes already included in the models, but low confidence that there are no important ones still omitted).

There is no confidence at all about any statements about future CO$_2$ uptake by shelf waters.

CITATION

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