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THE IMPACT OF RISING ATMOSPHERIC CO_2 LEVELS AND RESULTING OCEAN ACIDIFICATION TO THE PHYSICAL (SOLUBILITY) OCEAN PUMP OF CO_2.

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Abstract

An alternative measure of the ocean's carbonate buffer system efficiency to absorb CO_2 from the atmosphere is proposed. Instead of the Revelle factor R = (ΔCO2/CO2)/(ΔDIC/DIC) = (DIC/CO2)/ (ΔDIC/ΔCO2) the sensitivity S = (ΔDIC/ΔCO2) is preferable because it gives directly the change ΔDIC of the concentration of DIC in the seawater caused by the change ΔCO2 of carbon dioxide in the atmosphere. To this end the DIC concentration of seawater at temperature T in equilibrium with a defined CO_2 level in the surrounding atmosphere is calculated by use of the geochemical program PHREEQC. From the function DIC(CO2,T) one obtains by differentiation the sensitivity S = dDIC/dCO2 = ΔDIC/ΔCO2 and also the Revelle factor R. Using S as the change of the ocean's buffer capacity reveals a better insight of its future evolution than using the Revelle factor R.

One finds that the buffer capacity S has declined by about 30% from 1945 to present and that its future decline from 400 to 600 ppm will be a further 30%. By calculating the uptake of CO_2 of his equilibrium pump an upper value of 1.3 Gigatons/year is obtained, small in comparison to the 10 Gigatons/year absorbed by the ocean at present. The Revelle factor R at present is calculated R = 13 and rises to 18 at a CO_2 level of 800 ppm. This increase of R

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has been interpreted as indication of the collapse of the solubility pump. S and R, however, are defined from equilibrium chemistry and are a measure of the CO_2 absorbed by the ocean's upper mixed layer by increase of the CO_2 level in the atmosphere without regarding its sinking into the deep-ocean by the thermohaline circulation. The difference ΔDIC between the actual value and the value at 280 ppm is transported into the deep-ocean by the global meridional conveyor belt. ΔDIC increases with increasing CO_2 level. At 280 ppm the system ocean-atmosphere is in equilibrium and the sink is zero. At 400 ppm a value of about 1.9 Gtons/year is estimated that increases to 3.9 Gtons/year at 600 ppm and to 5 Gtons/year at 800 ppm. At present CO_2 level increase of 2ppm/year 10 Gtons/year are absorbed by the ocean. The solubility pump contributes 3.2 Gtons/year: 1.3 Gtons/year by equilibrium absorption into the mixed layer and 1.9 Gtons/yeat by thermohaline circulation. At 600 ppm the total sink is 4.6 Gtons/year and at 800 ppm 5.5 Gtons/year. To conclude, the solubility pump is not endangered by ocean acidification. In contrast, it increases with increasing CO_2 level of the atmosphere to yield significant contribution.

1. Introduction

Only one half of anthropogenic CO_2 emitted remains in the atmosphere. About one quarter is absorbed by the land sink via vegetation. The remaining quarter sinks into the ocean by the biological pump and the physical (solubility pump) **(**Friedlingstein et al., 2022**).** The ocean CO_2 sink has increased steadily with rising CO_2 level since the beginning of industrialisation. As an example, CO_2 level of 317 ppm in 1960 raised to 420 ppm in 2021 and accordingly the ocean sink from 1.1 ± 0.4 GtC/yr in 1960 to 2.8 ± 0.4 GtC/ y during 2021 (Friedlingstein et al., 2022**).** Thus, the ocean sink has increased proportional to the rise in atmospheric CO_2.To predict the future evolution of the CO_2-concentation (ppm) in the atmosphere by models

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one has to know whether this increase will be permanent. One part of the oceanic sink is the solubility pump that transports dissolved inorganic carbon (DIC) in equilibrium with the partial pressure p_{CO2} in the atmosphere (0.0001 atm ≙ 100 ppm) into the deep ocean. The future effectivity of this physical pump has been questioned because with increasing acidification of the ocean its buffering capacity decreases. This is commonly expressed by the Revelle factor R (Zeebe and Wolf-Gladrow, 2001, Eglestone et al., 2010).

$R = (\Delta DIC/DIC)/(\Delta CO2/CO2) = (\Delta DIC/\Delta CO2)/(DIC/CO2)$.

ΔDIC is the change in concentration DIC caused by a small increase ΔCO2 of the concentration CO_2 in the atmosphere. CO_2 and DIC are the corresponding concentrations. However, the Revelle factor is used mostly only qualitatively stating that increasing values of R indicate weakening of the buffer capacity (e.g., Climate Change 2007: The Physical Science Basis. AR4 IPPC, Bates and Johnson, 2020). A more appropriate measure, the sensitivity

$S = \Delta DIC/\Delta CO2$ has not been used in the scientific community. Middelburg et al., 2020 state: "there are few studies where buffer and/or sensitivity factors are being used, except for the well-known Revelle factor." To judge quantitively the decrease of buffer capacity that gives the amount of DIC increase by reaction of CO_2 to HCO_3^- and CO_3^- the evolution of sensitivity S in dependence on the CO_2 level in the atmosphere is a better alternative. To this end I calculate using the geochemical program PHREEQC (Parkhurst and Appelo, 2013) the chemical composition of sea water in chemical equilibrium with CO_2 of defined partial pressure p_{CO2} (ppm) in the surrounding atmosphere at defined temperature T. This way DIC(pCO2,T) as a function of p_{CO2} and T is obtained. By differentiation one gets $dDIC/dpCO2 = \Delta DIC/\Delta CO2 = S$ at defined temperature. From this I discuss the decrease of buffer capacity with increasing p_{CO2}. I report the Revelle factor R as a function of S to enable quantitative

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arguments using the Revelle factor R. This equilibrium pump does not consider the overturning circulation of the ocean that transports the water of the mixed zone into deep-ocean. This transport pump increases steadily with increasing p_{CO2}. The physical pump is the sum of the sink by the equilibrium pump and the overturning transport pump. It increases steadily to yield significant contributions.

Methods

The input file of the program PHREEQC is shown in Table 1. The first block `SOLUTION 1` defines the composition of sea water including major elements and boron. The second block EQUILIBRIUM_PHASES equilibrates this solution with gaseous CO_2 of the surrounding atmosphere. Input parameters are temperature "temp" in °C and CO2(g) as log(p_{CO2}) where p_{CO2} is in atm.

From the output file one can read pH and extract the concentrations of DIC (C(4)) and its

```
SOLUTION 1  Seawater
units ppm
pH 8.22
pe 8.451
density 1.023
temp 5
Ca 412.3
Mg 1291.8
Na 10768.0
K  399.1
Si 4.28
Cl 19353.0
B  4.5
Alkalinity 141.682
     as HCO3
S(6) 2712.0
EQUILIBRIUM_PHASES
CO2(ag)  -2.921
END
```

Table 1: Input file of PHREEQC

```
        pH = 7.715

 DIC C(4)        2.425e-03

HCO3-           1.753e-03
 MgHCO3+         3.129e-04
 NaHCO3          2.253e-04
 CO2             6.588e-05
 CaHCO3+         3.420e-05

   8.017e-06
 NaCO3 MgCO3
    1.542e-05
 CO3-2      -
    5.031e-06
 CaCO3           4.984e-06
```

Table 2: Output results

species in mol/kg. The program includes ion pairs with Ca and Mg. $MgHCO_3^+$ and $NaHCO_3$

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occur in considerable concentrations. In programs that do not include ion pairs these are included as HCO_3^-. I have calculated DIC and pH from CO_2 levels of 300 ppm in steps of 33ppm up to 800 ppm. The data points were transferred to the program Origin. Then they were fitted to a 5th order polynomial (R-square = 0.99995; SD = $3{,}3 \cdot 10^{-4}$; $p<10^{-4}$) to smooth the data for differentiation performed by the program. The figures were created by the graphics of Origin.

3. Results

Fig.1 represents the results for DIC at fixed temperature T = 15°C (solid line). The dashed line depicts the path where according to the increasing CO_2 level the temperature increases

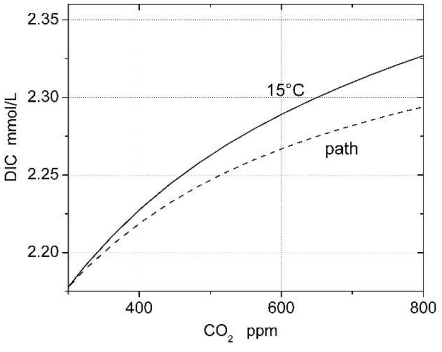

Fig. 1: DIC at fixed temperature of T = 15°C (solid line). The dashed line depicts DIC when temperature changes with increasing CO_2

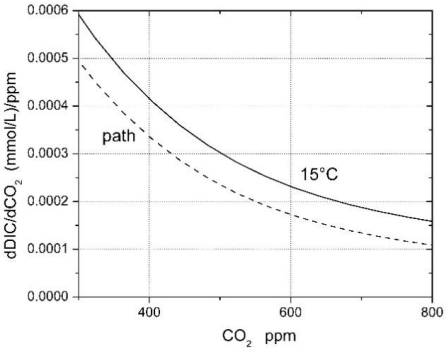

Fig. 2: Sensitivity S = dDIC/dCO2 for fixed temperature (solid line) and the path (dashed line) taking into account temperature increase with increasing CO_2 level. See text.

linearly by 0.01 °C per 1ppm increase of CO_2 level corresponding to their linear correlation obtained from NASA data of temperature and CO_2 level. The curve starts at T = 15°C, 300 ppm with steps of 33 ppm and 0.34°C and ends at 800 ppm and T = 19.1 C. Due to the rising temperature DIC is reduced slightly in comparison to fixed temperature a1 15 °C. Fig 2 depicts the sensitivity S = dDIC/dCO2 obtained from differentiation of the curves in Fig. 1.

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dDIC is the change in the concentration of DIC in mmol/L that is caused by an increase of CO_2 by dCO_2 in ppm. This change can be converted as change of the aqueous CO_2 concentration c_{aq} in the liquid by Henry's law $c_{aq} = K_H \cdot p_{CO2}$. At 15°C for sea water, $K_H = 0.04$ mol/atm (Zeebe and Wolf-Gladrow,2001). For 1ppm the change $dc_{aq} = 4 \cdot 10^{-5}$ mmol CO_2^{aq}. The corresponding change dDIC = S·1ppm = 0.0004 mmol DIC. Defining S*in units of mmolDIC/mmolCO_2^{aq} this way S*= 0.0004/0.00004 mmolDIC/mmol CO_2^{aq} = 10

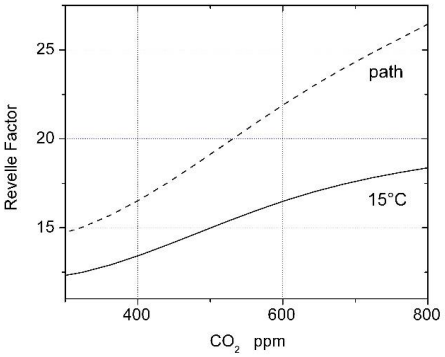

Fig. 3: Revelle factor for fixed temperature (solid line) and path (dashed line).

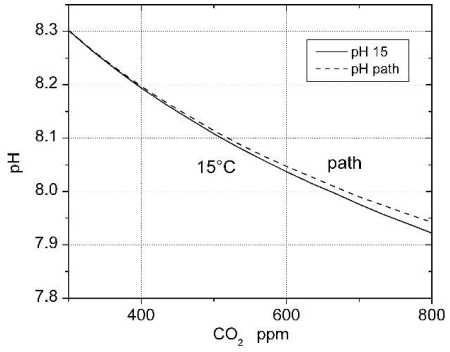

Fig. 4: pH for fixed temperature (solid line) and path (dashed line).

mmolDIC/mmolCO_2^{aq} at 400 ppm. This means that 10 units CO_2 have been absorbed of which 9 units have reacted to carbonates. For low pH < 4 where all DIC is in CO_2^{aq}, S* = 1. At 15°C the value of S = 0.0001 corresponds to value S* = 2.5. Note that this conversion depends on temperature due to the temperature dependence of K_H (0.051 at 5°C, 0.038 at 15°C. and 0.029 at 5°C). Both sensitivity curves show a steady drastic decline of the buffering capacity from 0.0006 to 0.00016 (mmol/L)/ppm at fixed temperature and from 0.0005 to 0.00011 (mmol/L)/ppm for the path. Thus, the reduction by doubling CO_2 from 300 ppm to 600 ppm means a reduction to 42 % at fixed temperature and 33 % for the path.

The corresponding Revelle factors R = (DIC/CO2)/(dDIC/dCO2) are shown in Fig. 3. They

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illustrate why the Revelle factor cannot be used easily as quantitative measure because the reduction of buffer capacity is by its change and not by its absolute value. Therefore, one has to know the end values. In contrast, sensitivity S gives the reduction from the known initial value. In other words, the large background of R at 300 ppm prevents a reasonable interpretation. Finally, in Fig. 4 acidification of ocean, the reason for declining buffer capacity is shown as pH versus CO_2 level. pH drops almost linearly with CO_2 level from pH = 8.3 at 300 ppm to 7.9 at 800 ppm. There is little difference between constant temperature at 15°C and the path regarding global warming. The change in pH is close to the projection of Jiang et al., 2019 using the RCP 6.0 scenario of IPCC. This holds also for the change of the Revelle factor R in Fig. 3.

4. Discussion

To obtain some overview on the variability of sensitivity S and Revelle factors R in Fig. 5 one finds DIC for 5, 15, and 25°C respectively. The corresponding sensitivities S are shown in Fig. 6 and the Revelle factors are depicted in Fig. 7. For completion pH is illustrated in Fig. 8.

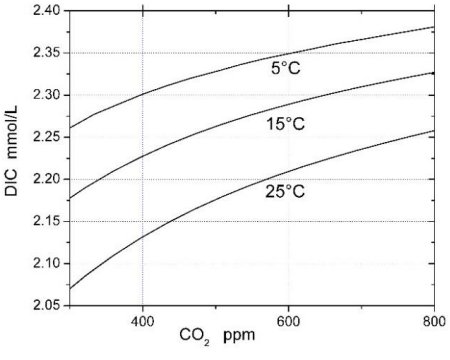

Fig. 5: DIC concentration for various temperatures

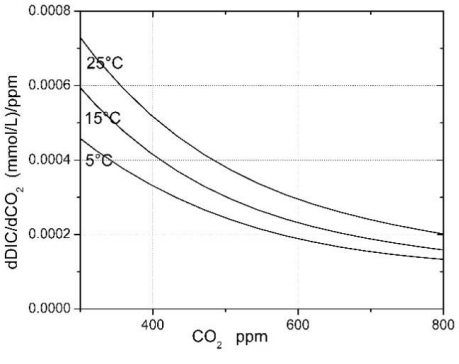

Fig. 6: Sensitivity S = dDIC/dCO2 for various temperatures

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At fixed CO_2 the DIC concentration (Fig. 5) decreases with temperature whereas the sensitivity S increases as can be seen from the slopes increasing with rising temperature. These slopes are shown as S = dDIC/dCO2 in Fig. 6. S increases with rising temperature. As one can read from Fig. 6 an increase of temperature by 5°C causes a reduction of the initial value at 15°C by about 10% for all CO_2 levels. The impact of changing CO_2 level by far exceeds that of increasing temperature.

S decreases with increasing CO_2 level. It is important to note that one finds a reduction by 36 % at the beginning from 300 to 420 ppm, corresponding to the time from 1945 to 2021. Further reduction from 400 to 500 ppm is 16 % and continues to decrease further on for all temperatures. This is in contrast to the opposite behaviour of the Revelle factor in Fig. 7. One finds a small increase at the beginning up to 400 ppm followed by rise about twice of the initial one for CO_2 between 400 to 600 ppm, valid for all temperatures. Thus, using S as measure for impact to the oceans buffer capacity leads to conflictive conclusion about future

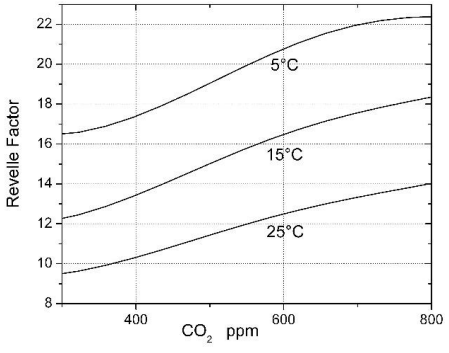

Fig. 7: Revelle factor for various temperatures

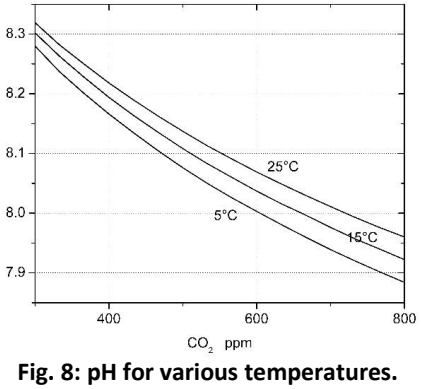

Fig. 8: pH for various temperatures.

evolution with consequences in defining pathways for CO_2 emissions in climate change policy. At present public policy seems to be convinced that at least the physical ocean pump will fail in the near future. Although the mixed layers capacity has been reduced by about 30% of its initial value for all temperatures during 1945 (300ppm) to 2015 (400ppm). The

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ocean sink (Friedlingstein et al., 2022), however has continuously increased during this time span. This leads to the conjecture that the physical sink into the mixed layer may not contribute as significantly to the total ocean sink as thought by using the concept of equilibrium chemistry (Revelle factor).

Finally, to relate sensitivity S to Revelle factor R, Fig. 9 illustrates R as a function of S.

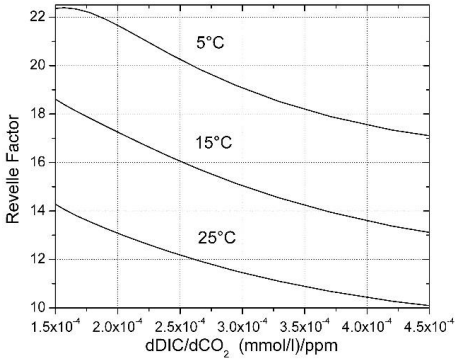

Fig. 9: The Revelle factors R in relation to the sensitivity S for various temperatures

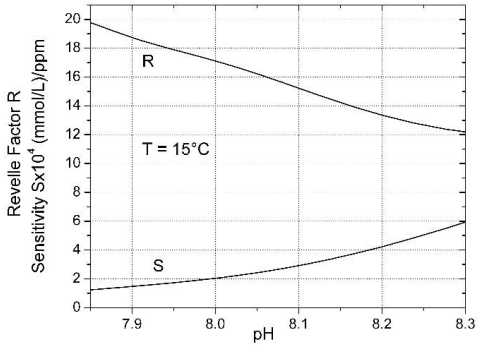

Fig. 10: The Revelle factor R and sensitivity S as function of pH at 15°C

It is obvious why using S should be preferred. If S changes from $1.5 \cdot 10^{-4}$ to $4.5 \cdot 10^{-4}$ by 200 % the corresponding chage in R is only about 40 % for 25°C and 20% for 5°C. Therefore, S gives a more realistic view. Fig. 10 shows R and S as function of pH at 15°C. R changes from 12 to 20 with pH dcreasing from 8.3 to 7.85. But, in contrast to the sensitivity from its value no direct meaning can be derived. From its defition a simple relation is: R = 2.27/(CO2·S) because DIC ≈ 2.27 mmol/L remains constant within a few percent (see Fig. 1 and Fig. 5). From this one may understand why R is used only qualititavely to judge ocean's physical pump buffer capacity.

Using the DIC data one can estimate the upper limit of the present CO_2 flux from the atmosphere to the ocean's mixed layer. I calculate the volume V_1 of the upper 1 meter of the mixed layer $V_1 = 0.71 \cdot 4\pi R^2 \cdot 1\ m^3 = 3.6 \cdot 10^{17}$ L. R is Earth radius and 0.71 ocean coverage. The

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amount M_1 of DIC that can be absorbed with a sensitivity $S_1 = 10^{-7}$(mol/L)/ppm is $M_1 = V_1 \cdot S_1$ mol/ppm. Consequently, the amount M_t absorbed by a mixed layer with depth t(m) and a change of n ppm CO_2 is $M_t = M_1 \cdot t \cdot s \cdot n$ mol CO_2 when sensitivity $S = s \cdot S_1$. Converting to g CO_2 one has to multiply by the molecular weight 44 g/mol of CO_2 to obtain

$M_t = M_1 \cdot t \cdot s \cdot n$ mol$\cdot$44g/mol $= M_1 \cdot t \cdot s \cdot n \cdot 44$ (g).

A reasonable estimation of the mixed layer depth t is 100 m (de Boyer et al., 2004, Boyer et al., 2022, Birol Kara et al., 2000, Doney et al., 2004). At present the increase of CO_2 is 2 ppm/year (n = 2) and (s = 4). Using these numbers, one finds $M_t =$ 1.3Gigatons/year. The value of s = 4 corresponds to a temperature of 15°C at 420 ppm (see Fig. 6). This assumption is reasonable because oceans temperature is distributed between 25° at the equator to 5°C in the polar oceans.

Another argument must also be considered. Carbon is absorbed by the ocean where water sinks to the deep ocean. At regions of upwelling water rich in CO_2, however, CO_2 is released into the atmosphere (Landschützer et al., 2014, Crisp et al., 2022). This water outgasses CO_2 into an atmosphere with higher partial pressure. This causes a reduced flux of outgassing and the difference of outgassing between higher and lower partial pressure at the intake acts as effective influx in upwelling regions and justifies the assumption.

It must be stressed that the flux calculated so far by equilibrium chemistry represents the capacity to absorb CO_2 from the atmosphere by a stagnant isolated mixed layer that does not sink into depth. Therefore, this sink is caused by equilibrium chemistry and could be termed as equilibrium sink (pump). This pump declines with increasing acidification of the ocean. At pH < 4 the only existing carbonate species are aqueous CO_2 and H_2CO_3. Therefore, the absorption of CO_2 is governed by Henry's law. Therefore, dDIC/dCO2 = K_H and stays constant with further decreasing pH. At 15°C dDIC/dCO2 = $4 \cdot 10^{-5}$ mmol/ppm. This

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corresponds to a flux of 0.13 Gt/year, an almost total breakdown of the mixed layer's capacity to absorb CO_2.

This, however, does not mean that the physical pump breaks down as has been concluded from the increase of the Revelle factor. In IPCC AR4 one finds: "The ocean's capacity to buffer increasing atmospheric CO_2 will decline in the future as ocean surface pCO_2 increases (Figure 7.11a). This anticipated change is certain, with potentially severe consequences." (Denman et al., 2007).

The total CO_2 sink consists of two parts: the equilibrium sink as already stated and the transport sink. This is governed by the global meridional overturning circulation where surface waters of the mixed layer flow from the equator to the polar regions and sink there into the deep ocean by thermohaline circulation. In the North Atlantic deep water formation is 15±2 Sv (1 Sv = 10^6 m^3/s) and 21±6 Sv in the southern ocean (Ganachaud and Wunsch, 2000, Rahmstorf, 2002). These waters have cooled to low temperatures (about 5°C) when they sink. They transfer the CO_2 in the mixed layer that contains also the anthropogenic carbon into deep-ocean. These waters are replaced by upwelling waters back to the surface without anthropogenic carbon (Terhaar et al., 2022) that readily absorb CO_2 from the atmosphere until equilibrium is established.

Dividing the volume V_{mix} of the mixed layer by the global formation of deep water of 36±6 Sv one obtains, τ_{drain}, the time needed to drain that layer into the ocean as 57 years. The time for chemical equilibration to a change of atmospheric CO_2 is on the order of 1 year (Jones et al., 2014). Therefore, DIC in the mixed layer is in equilibrium with the CO_2 in the atmosphere as given in Fig.5. At a CO_2 level of 280 ppm the flux of CO_2 into the ocean is zero and the system is in equilibrium (Friedlingstein et al., 2022). With increasing CO_2 level, the deviation of DIC equilibrium concentration is given by $(DIC_{ppm} - DIC_{280}) = \Delta DIC_{ocean}$. ΔDIC_{ocean} represents

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the amount of anthropogenic carbon absorbed into the mixed layer since the onset of industrialisation. The flux F_{ocean} into the ocean is given by $\Delta DIC \cdot V_{mix} / \tau_{drain} = F_{ocean}$ in Gtons/year. At 400 ppm one finds a value of $F_{ocean} = 1.9$ Gtons/year

Fig. 9 depicts F_{ocean} in dependence on the CO_2 level. F_{ocean} does not increase linearly with CO_2 level but increases with declining slope to 0.0087 Gtons/(year ppm) that stays constant for $p_{CO2} > 1$ atm as calculated by PHREEQC. This way for an increase of 1 ppm/year of CO_2 level, F_{ocean} increases by 0.0087 Gtons/year.

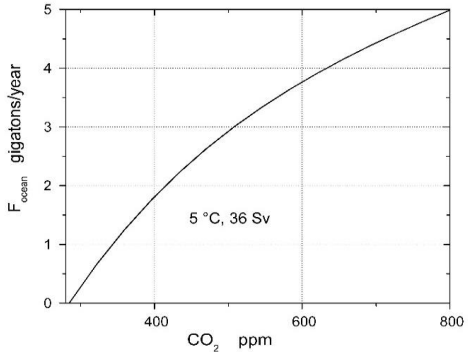

Fig. 11: Flux F_{ocean} into the ocean in dependence on CO_2 level

At present the total Ocean sink is 10 Gt/year. If at 400 ppm a total sink of 3.2 Gt/year is correct the contribution of the physical pump is relatively small. It is possible that the biological pump (Hauck and Völker, 2015, Riebesell et. al., 2007) compensates for this. In view of the fact that this estimation might be critiqued it should motivate further research and discussion in ongoing projects.

5. Conclusion

An alternative measure of the ocean's carbonate buffer to absorb CO_2 from the atmosphere is proposed. Instead of the Revelle factor R = (ΔCO2/CO2) /(ΔDIC/DIC) = (DIC/CO2)/ (ΔDIC/ΔCO2) the sensitivity S = (ΔDIC/ΔCO2) is preferable because it gives directly the change ΔDIC of the concentration of DIC in the seawater caused by the change ΔCO2 of carbon dioxide level in the atmosphere. To this end the DIC concentration of seawater in

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equilibrium with a defined CO_2 level in the surrounding atmosphere is calculated by use of the geochemical program PHREEQC. From the function DIC(CO2) by derivation one obtains the sensitivity S = dDIC/dCO2 = ΔDIC/ΔCO2 and also the Revelle factor R.

Using S, the change of the ocean's buffer capacity better insight of its future evolution is obtained than by use of the Revelle factor R.

S declines heavily since 1945 until it breaks down at CO_2 levels of 800ppm. One has to consider, however, that R and S are calculated by equilibrium chemistry that does not contain the sink caused by the thermohaline overturning circulation that transports the water of the mixed zone into deep-ocean. S therefore, gives the amount of carbon as ΔDIC that is stored in the mixed layer when the CO_2 level increases by ΔCO2.

The total solubility sink consists of two mechanisms: The equilibrium pump as described and the transport pump that is caused by the global meridional overturning circulation of 36 Sv. This transfers into deep-ocean the difference (DIC_{ppm}- DIC_{280}) = ΔDIC_{ocean} that has been accumulated in the mixed layer from onset of industrialisation to the actual CO_2 level.

This sink increases continuously replacing the failure of the equilibrium pump. At 400 ppm the total sink is 1.9, at 600 ppm it is 3.8 and at 800 ppm it amounts to 5 Gtons/year depending solely on the CO_2 level in the atmosphere for ppm > 600.

To conclude, the total solubility pump is not endangered by ocean acidification. In contrast, it increases with increasing CO_2 level of the atmosphere to yield significant contribution to remove anthropogenic CO_2 from the atmosphere into deep-ocean.

I declare that I do not have any competing interests.

References

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Bates, N.R., Johnson, R.J. Acceleration of ocean warming, salinification, deoxygenation and acidification in the surface subtropical North Atlantic Ocean. *Commun Earth Environ* 1, 33 2020. https://doi.org/10.1038/s43247-020-00030-5

Crisp D., Dolman H., Tanhua T.,McKinley G. A., Hauck J., Bastos A., Sitch S., Eggleston S., Aich V. How Well Do We Understand the Land-Ocean-Atmosphere Carbon Cycle?, Reviews of Geophysics / Volume 60, Issue 2 / e2021RG000736, 2022 https://doi.org/10.1029/2021RG000736

de Boyer Montegut Clement, Gurvan M., Fischer A. S., Lazar A., Iudicone D. Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology. *Journal Of Geophysical Research-oceans*, 109(C12/C12003), 1-20.2004 https://doi.org/10.1029/2004JC002378

de Boyer Montégut Clément (2022). Mixed layer depth climatology computed with a density threshold criterion of 0.03kg/m3 from 10 m depth value. SEANOE. https://doi.org/10.17882/91774

Denman, K.L., G. Brasseur, A. Chidthaisong, P. Ciais, P.M. Cox, R.E. Dickinson, D. Hauglustaine, C. Heinze, E. Holland, D. Jacob, U. Lohmann, S Ramachandran, P.L. da Silva Dias, S.C. Wofsy and X. Zhang, 2007: Couplings Between Changes in the Climate System and Biogeochemistry. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA .2007

Doney S. C. et al., Evaluating global ocean carbon models: The importance of realistic physics, GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 18, GB3017, 2004

Egleston E. S., Sabine C., Francois M. M., Morel F. M. M., Revelle revisited: Buffer factors that quantify the response of ocean chemistry to changes in DIC and alkalinity. Global Biogeochemical Cycles, Global Biogeochemical Cycles, Volume 24, Issue 1, 2010 https://doi.org/10.1029/2008GB003407

Friedlingstein P. 2015 Carbon cycle feedbacks and future climate change. Phil. Trans. R. Soc. A 373: 20140421. 2015

Ganachaud, A. & Wunsch, C. Improved estimates of global ocean circulation, heat transport and mixing from hydrographic data. Nature 408, 453–457 (2000).

Hauck J., Völker C. Rising atmospheric CO_2 leads to large impact of biology on Southern Ocean CO_2 uptake via changes of the Revelle factor Geophysical Research Letters Volume 42, Issue 5 p. 1459-1464, 2015 https://doi.org/10.1002/2015GL063070

Jiang L-Q., Carter B.R., Feely R. A., Lauvse S. K., Olsen A. Surface Ocean pH and buffer capacity: past, present and future. Scientific Reports, 9:18624, 2019 https://doi.org/10.1038/s41598-019-55039-4

Jones, D. C., T. Ito, Y. Takano, and W.-C. Hsu (2014), Spatial and seasonal variability of the air-sea equilibration timescale of carbon dioxide, Global Biogeochem. Cycles, 28, 1163–1178, doi:10.1002/2014GB004813

Kara A. B., Peter A. Rochford, Harley E. Hurlburt. An optimal definition for ocean mixed layer

https://doi.org/10.5194/egusphere-2023-1004
Preprint. Discussion started: 30 May 2023

305 Landschützer P., Gruber N., Bakker D. C. E., Schuster. Recent variability of the global ocean
306 carbon sink. Global Biogeochemical Cycles, 28, 927-949, 2014
307 Köhler P., Hauck J., Völker C., Wolf-Gladrow D. Interactive comment on "A simple model of
308 the anthropogenically forced CO_2 cycle" by W. Weber et al., Earth Syst. Dynam. Discuss., 6,
309 C813–C813, 2015. www.earth-syst-dynam-discuss.net/6/C813/2015/
310 Middelburg J. J., Soetaert K., Hagens M. Ocean Alkalinity, Buffering and Biogeochemical
311 Processes, Reviews of Geophysics, Volume 58, Issue 3 / 2020
312 https://doi.org/10.1029/2019RG000681
313 Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC
314 version 3—A computer program for speciation, batch-reaction, one-dimensional transport,
315 and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book
316 6, chap. A43, 497 p., available only at http://pubs.usgs.gov/tm/06/a43.
317 Rahmstorf S. Ocean circulation and climate during the past 120,000 years. 2002, NATURE
318 419, 207-214
319 Zhang X., 2007: Couplings Between Changes in the Climate System and Biogeochemistry. In:
320 Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the
321 Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S.,
322 D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)].
323 Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. 2007
324 Terhaar J., Frölicher T. L., Joos F. Observation-constrained estimates of the global ocean
325 carbon sink from Earth system models. Biogeosciences, 19, 4431–4457, 2022
326 https://doi.org/10.5194/bg-19-4431-2022
327 Zeebe R. E. and Wolf-Gladrow D. CO_2 IN SEAWATER: EQUILIBRIUM, KINETICS, ISOTOPES,
328 Elsevier Oceanography Series, 65, 2001

329