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Part 1: Basic elements for avoiding greenhouse gases and generating climate-neutral energy (technical toolbox)

Chapter 2-11

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2.11 Oceans as a sink for anthropogenic CO₂

2.11.1 Introduction

The world's oceans are the largest carbon reservoir on earth and one of the most important buffers for climatic changes in the atmosphere.

They are able to absorb and store large amounts of anthropogenic CO₂ emissions. It is estimated that between 1994 and 2007, approximately 30 % of these CO₂ emissions were absorbed by the world's oceans. This corresponds to 34 ± 4 Gt CO₂ or an average of 2.6 ± 0.3 Gt CO₂ per year⁵⁷⁸.

Figure 180⁵⁷⁹ and Figure 181⁵⁸⁰ show simplified global ocean currents and the regional distribution of CO₂ exchange with the atmosphere.



Figure 180: Global ocean currents;

Source:Ocean-Climate (2022)

 ⁵⁷⁸ Cf. Gruber (2019), The averaging is unclear: 34 Gt/13 years equals 2.6 Gt/year, the range is probably 0.3 Gt/year).
⁵⁷⁹ Cf. Ocean-Climate (2022)

⁵⁸⁰ Cf. CDRmare (2022)



Netto Kohlendioxid-Fluss zwischen Atmosphäre und Meer im Zeitraum von 1994 bis 2007

Figure 181: Regional CO₂ uptake and release by the oceans;

Source: CDRMare (2022)

 CO_2 uptake takes place mainly in the colder regions of the North Atlantic and Pacific and in the upper water layers due to the higher physical solubility and gas exchange. In the warmer, more tropical regions, on the other hand, CO_2 is released into the atmosphere.

CO₂ partial pressure, temperature, salinity, water stratification and currents play an important, but in many areas still unexplored, complex role.

For the observation period from 1994 to 2007, various model calculations show in Table 45 show good agreement with the recorded CO_2 quantities.⁵⁸¹

The quantification and extrapolation of CO₂ uptake with increasing CO₂ content of the atmosphere, i.e. CO₂ partial pressure, depends on many parameters such as temperature, salinity, pH value, underwater biodiversity and ocean currents and stratification, and is therefore difficult to calculate, verify and thus assess.

⁵⁸¹ Cf. Watson (2020)

Table 45: Quantities of CO absorbed by oceans in the years 1994 to 2007₂ according to two model calculations, data in PgC (Petagram of Carbon) ; ⁵⁸²

	Atlantic	Pacific	Indian	Other regions	Global	
Cumulative CO ₂ uptake through surface (–ve is into ocean) July 1994 to June 2007 (PgC, $\pm 2\sigma$)						
North	-5.68 ± 0.97	-6.60 ± 0.90	+1.16 ± 0.43	-1.56 ± 0.8	-12.7 ± 1.6	
South	-3.22 ± 0.91	-3.43 ± 4.6	-7.41 ± 0.96	-	-14.1 ± 4.6	
Total	-8.91 ± 1.50	-10.04 ± 4.3	-6.25 ± 1.20	-	-26.8 ± 3.4	
Gruber et al. ¹⁷ estimates of inventory increase 1994–2007 (PgC)						
North	6.0 ± 0.4	5.2 ± 0.6	0.8 ± 0.4	1.5 ± 0.6	13.5 ± 1.0	
South	5.9 ± 1.2	8.0 ± 1.2	6.3 ± 3.4	-	20.1 ± 3.8	
Total	11.9 ± 1.3	13.2 ± 1.3	7.1 ± 3.4	-	33.7 ± 4.0	

Source Gruber (2019)

Nevertheless, various models in Figure 182 show the further development of annual CO_2 uptake up to the year 2018 relatively consistently.⁵⁸¹ The red area shows the average of the years 1994 - 2007 (see Table 45), the black line a consensus range of various models, the broken lines two other calculations.

There is a consistent trend of increasing uptake of anthropogenic CO_2 , which is probably related to the increasing CO_2 partial pressure. The opposite effect of reduced CO_2 solubility with rising water temperatures is probably overcompensated here, since the change in water temperature occurs more slowly than the increase in CO_2 content or partial pressure of the atmosphere due to the high heat capacity of the oceans.

With all the uncertainties of the models, the annual CO_2 uptake is in the order of <u>3 - 4 Gt carbon</u> or <u>10 - 14 Gt</u> CO_2 . How long the trend of increasing CO_2 uptake will last, however, cannot be predicted at present.

⁵⁸² 1 PgC = 44/12 PgCO₂



Figure 182: Development of anthropogenic CO₂ uptake until 2018 based on various calculation models (1 PgC petagram corresponds to 1 gigatonne); source: Watson et al., 2020

2.11.2 Mechanism of natural storage of CO₂ in the oceans

Up to a water depth of several hundred metres, CO_2 is gaseous despite the water pressure increasing with depth and dissolves in water until saturation. At a depth of approx. 500 to 2,700 m, CO_2 is liquid, but still has a lower density than the surrounding salt water, so it also rises when supersaturated. At water depths above 3,000 m, the liquid CO_2 has a higher density than the surrounding salt water and would form " CO_2 ponds" or "lakes" on the seabed if it were present in sufficient quantities. ⁵⁸³ Depending on temperature and salinity, the formation of solid CO_2 hydrates is possible at shallower depths. The formation of hydrates in deep layers is reversible depending on the ambient conditions, so hydrates are not sustainable CO_2 reservoirs.

The phase diagram of the system (pure) water/ CO_2 as a function of pressure and temperature shows Figure 183.⁵⁸⁴ The role of the salinity in the water cannot be seen in this diagram. However, the influence of salinity in seawater is of minor importance compared to the influence of water temperature and CO_2 partial pressure, (see Table 46).⁵⁸⁵

- 583 Cf. Hume (2018)
- ⁵⁸⁴ Cf. Nasa (2022)

⁵⁸⁵ Cf. Li (1971)



Figure 183: Phase diagram of CO₂ in water as a function of pressure and temperature;

Source: Nasa (2022)

Table 46: Solubility constants of CO_2 in water, NaCl solutions and seawater (in 10^{-4} mol/litre/atm);

C1 ‰	t,°C				
	0.7	4.0	10.2	20.0	30.0
0	750.1	660.3	530.2	391.1	299.7
10.0			486.3		
20.0		552.6	448.2	335.9	261.4
29.0		508.6	416.2	313.8	246.3
0.6413 m NaCl		554.7		335.8	261.8

Source: Li & Tsui, 1971

Since the water depths of the oceans are more than 70 % above 3,000 m, there is a huge potential for CO_2 storage of a calculated 4,000 to 10,000 Gt CO $_2^{586}$, whereby the associated lowering of the p_H value would have drastic consequences for all marine organisms such as corals, marine snails and mussels.

Basically, a distinction is made between two storage mechanisms, the "physical and the biological pump", see Figure 184.⁵⁸⁷ The storage quantities are influenced by a so-called "chemical buffer" and a "biological buffer" beyond the purely physical solubility of CO₂.

Both the formation of inorganic sediments in the form of carbonates and the decaying and sedimenting biomass formed by photosynthesis contribute to permanent CO₂ storage.

CO₂ uptake by physical solubility in seawater depends not only on the CO₂ partial pressure (i.e. the CO_2 content of the atmosphere) and the water temperature, but also on the pH value and, to a lesser extent, the salinity of the seawater.

Cold water in the lower ocean layers dissolves more carbon dioxide, and at the same time the density of the colder water increases, causing the CO_2 -rich water to sink into deeper layers. However, this is only a reversible effect due to ocean currents and the associated water exchange.

It is true for all gases that their solubility decreases with increasing temperature and salt content but increases with increasing pressure. The CO₂ solubility in water is two orders of magnitude higher than that of oxygen, for example, see Table 47⁵⁸⁸ and Figure 185. ⁵⁸⁹



Figure 184: Biological and physical pump for the storage of CO₂ in the oceans⁵⁸⁹

⁵⁸⁷ Cf. www.worldbank.org/en/news/feature/2022/02/08/"what-you-need-to-know-about-oceans-andclimate-change", accessed 22.11.2022 ⁵⁸⁸ Cf. School of Chemistry (2022)

⁵⁸⁹ Cf. Lohninger (n.d.)

Water temperature (°C)	0	20	30	40	50
Solubility Oxygen in g/kg	0,0694	0,0432	0,0308	0,0227	0,0138
Solubility CO ₂ in g/kg	3,35	1,69	0,97	0,58	

Table 47: Solubility (g/kg) of CO2 and of oxygen in water at 1013 mbar



Figure 185: CO₂ solubility in (pure) water at normal pressure as a function of water temperature; source: ttps://prozesstechnik.industrie.de/chemie/kein-schaden-am-kessel/#slider-intro-2

2.11.3 Chemical and biological buffer

2.11.3.1 Chemical buffer

More than 90 % of the CO₂ dissolved in seawater is present as hydrogen carbonate, about 8 % as carbonate and only about 1 % as a physical CO₂ solution.

Most of the dissolved inorganic carbon in the ocean, i.e. 91 %, is present as hydrogen carbonate, 8 % as carbonate and 1 % as physically dissolved CO_2 . The chemical equilibrium existing between these components:

 $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2 \text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^{-1} \leftrightarrow \text{H}^+ + \text{CO}_3^{2-1}$

is shifted by further CO_2 uptake, i.e. leads to the additional formation of hydrogen carbonate through the reaction of CO_2 with carbonate, with the effect of a decreasing CO_2 uptake capacity and lowering of the pH value (acidification). A side effect is also damage to the skeleton formation (calcium carbonate) of marine organisms.

2.11.3.2 Biological buffer

However, the atmospheric carbon dioxide dissolved in the oceanic surface layer is not only chemically transformed, but also bound by the photosynthesis of the phytoplankton. The carbon is absorbed in the form of carbon dioxide or hydrogen carbonate. This reduces the partial pressure of CO₂ in the upper water layer and thus promotes the uptake of carbon dioxide from the atmosphere. Gross primary production by oceanic phytoplankton is estimated at 103 Gt C per year, respiration (autotrophic respiration) at 58 Gt C and net primary production correspondingly at 45 Gt C per year. The resulting organic carbon bound in the phytoplankton is consumed by the zooplankton, with 34 Gt C per year being released again through heterotrophic respiration. The rest becomes sedimentary waste, either directly or indirectly.⁵⁹⁰

2.11.4 CO2 uptake by coastal vegetation

Salt marshes, mangrove forests, seagrass meadows, kelp forests and kelp forests offer additional potential for CO₂ absorption and sequestration. Including the intertidal zones, they account for approx. 0.2 % of the ocean surface and are capable of sequestering 5 - 30 times the amount of carbon compared to rainforests.

Salt marshes cover about 60,000 km² and can sequester 28 - 17,000 kg of carbon per hectare per year. The wide range in carbon sequestration is explained by regional conditions, tidal range and climatic environment.

Mangrove forests cover 170,000 km² (almost half the area of Germany) and can sequester 560 - 11,000 kg of carbon per hectare annually.

Seagrass meadows cover 317,000 km² (approx. 90 % of the area of Germany) and can store 25 - 1000 kg of carbon per hectare annually. Again calculated with an average value of 500 kg/ha, this results in a CO₂ sequestration of 0.016 Gt/a.

Seaweed forests cover 3.4 million km² (9 times the area of Germany) with an as yet unknown but certainly considerable carbon sequestration potential. All figures are taken from CDMare Fact Sheet Coastal Ecosystems.⁵⁹¹

The coastal regions are thus a smaller but nevertheless indispensable CO₂ reservoir with an approximate uptake potential of up to 0.9 Gt/year calculated from the above estimates, plus the contribution of kelp forests.

⁵⁹⁰ IPCC (2001)

⁵⁹¹ Cf. CDmare (2022a)

2.11.5 Artificial CO₂ storage (Ocean Carbon Sequestration - OCR)

The known Carbon Capture and Storage (CCS) projects include, in the case of deep injection of CO_2 , storage of liquid CO_2 in corresponding water depths, injection into offshore oil and gas reservoirs and, in the case of corresponding basaltic rock formations, also mineralisation.

For example, BASF subsidiary Wintershall is planning to inject about 40 Mt CO₂ per year in the Norwegian sector of the North Sea with the Norwegian Horisont Energi. ⁵⁹²

Because of the very low and slow gas exchange between the atmosphere and seawater, because of the large uptake potential and because of expected low impacts due to acidification, sequestration of CO_2 in ocean depths above 4,000 m is also propagated, but not yet practised on a large scale. For example, the Sunda Trench could absorb an estimated 19,000 Gt, the Puerto Rica Trench 24,000 Gt of CO_2 .⁵⁹³

Whether such an option will ever meet with acceptance, despite its huge potential, is unclear due to the lack of knowledge about processes and long-term effects in the deep sea.



Figure 186: CO2 -deep injection into the sea

⁵⁹² Message from Redaktionsnetzwerk Deutschland, 30.11.2022

⁵⁹³ Goldthorpe (2017)

2.11.6 Summary

The annual CO₂ uptake capacity of the oceans is of a relevant order of magnitude at approx. 3 - 4 Gt carbon (10 - 14 Gt CO₂). A current accounting of anthropogenic CO₂ emissions shows that the oceans absorb about 26 % of the emissions, a similar order of magnitude to terrestrial CO₂ uptake (see Figure 187).

However, the long-term uptake capacity and associated negative effects on the ocean ecosystem are difficult to predict and still largely unexplored.

Active transport of CO_2 to depths below 3,000 - 4,000 m is not taken into account in the calculated orders of magnitude. There could be a significant opportunity for CCS (Carbon Capture and Storage) if long-term effects are better researched and this option finds social acceptance.

In the context of the GES model, the oceans represent an upscale potential for the 10 Gt CO₂ calculated in the terrestrial nature-based solutions domain.



Figure 187: Balance of global CO₂ emission and uptake on an annual average 2012 - 2021; Source Friedlingstein (2022)