CO₂ sequestration in the ocean

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ERCA, Grenoble 3 February 2010

CO₂ emissions: A large scale geophysical experiment (Revelle & Suess, 1957)

"Human beings are now carrying out a large scale geophysical experiment of a kind that could not have happened in the past nor be reproduced in the future."

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The 2°C warming target CO_2 emissions: less than 205 Gt C until 2050



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Malte Meinshausen¹, Nicolai Meinshausen², William Hare^{1,3}, Sarah C. B. Raper⁴, Katja Frieler¹, Reto Knutti⁵, David J. Frame^{6,7} & Myles R. Allen⁷

Limiting cumulative CO₂ emissions over 2000–50 to 1,000 Gt CO₂ yields a 25% probability of warming exceeding 2 °C—and a limit of 1,440 Gt CO₂ yields a 50% probability—given a representative estimate of the distribution of climate system properties.

Between 2000 and 2050: < 1000 Gt $CO_2 = 273$ Gt C Between 2010 and 2050: < 750 Gt $CO_2 = 205$ Gt C Current emission: ≈ 9 Gt C yr-1 -> ≈ 20 years



It's not just warming: Ocean acidification



Wolf-Gladrow et al., Tellus, B51(2), 461-476, 1999.

Advantage for algae: higher CO_2 concentration

Problems for calcifying organisms: CaCO₃ dissolves at low pH

Physiology of marine organisms

Ecosystems: change in species assemblage & function

Significant decreases in ocean sound absorption -> noisier, whales



Limacina retroversa australis (pteropod, ca. 2 mm), Southern Ocean, aragonite (CaCO₃) (Foto: Wolf-Gladrow)



Humble is a small town in Texas.DON'T BE HUMBLE!From Life Magazine 1962.





EACH DAY HUMBLE SUPPLIES ENOUGH ENERGY TO MELT 7 MILLION TONS OF GLACIER!

the of these states and

This giant glacier has remained unmelted for centuries. Yet, the petroleum energy Humble supplies—it converted into heat—could melt it at the rate of 80 tons each second? To meet the nation's growing needs for energy, Humble has applied science to nature's resources to become America's Leading Energy Company. Working wonders with oil through research, Humble provides energy in many forms—to help heat our homes, power our transportation, and to furnish industry with a great variety of versatile chemicals. Stop at a Humble station for new Enco Extra gasoline, and see why the "Happy Motoring". Sign is the World's First Choice!

THE REAL PROPERTY.

America's Leading Energy company (thanks to Stephen Salter)





1. Motivation

- 2. The global carbon cycle
- 3. Approaches: ocean iron fertilization, silicate weathering, ... What is the potential? Will it be effective?
- 4. Final remarks







Why does CO_2 in the atmosphere-ocean system for the helmholtz behave so much differently than O_2 or N_2 ?

In contrast to N_2 and O_2 most C of the combined atmosphere-ocean system is dissolved in seawater. Why is CO_2 so different?

When CO_2 dissolves in seawater it reacts with water ($CO_2 + H_2O$) and forms H_2CO_3 (true carbonic acid) that dissociates into HCO_3^- (bicarbonate) and H^+ ('protons' in the slang of marine chemists).

-> Addition of CO_2 to the ocean leads to creation of H⁺ und thus to ocean acidification ('the other CO_2 problem').



Bjerrum plot (Zeebe & Wolf-Gladrow, 2001)



Ocean acidification: HCO_3^- , less CO_3^{2-}

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DIC distribution in the ocean Takahashi, T. 1989. The carbon dioxide puzzle. Oceanus, 32: 22-29.



Figure 1. Depth distribution of the total CO_2 concentration in the global oceans. NA & SA = North & South Atlantic; NP and SP = North and South Pacific; NI and SI = North and South Indian Oceans; and AA = Antarctic ocean. Inhomogeneous distribution: from < 2000 μ mol kg⁻¹ up to almost 2400 μ mol kg⁻¹, i.e. 20% variation

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- 1. Low concentrations in surface ocean.
- 2. Maxima at intermediate depths.
- 3. Increase from North Atlantic to Southern Ocean to North Pacific.

How to explain this distribution?



Which processes create inhomogeneous DICdistribution?I. Physical or solubility pump

Mixing in the ocean (up to 1000 years) is much slower than in the atmosphere (1 year between hemispheres)

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Pump: transport against the concentration gradient, i.e. from surface ocean to intermediate and deep layers.

1: Physical or solubility carbon pump:

The solubility of CO_2 is higher in cold than in warm water -> more CO_2 and DIC in cold water + circulation: deep water formation in cold regions, deep ocean is cold and rich in DIC



Most of the ocean is cold



The warm water sphere is restricted to a thin surface layer. ... most of the ocean is cold (< 5° C) and rich in DIC



eWOCE (Reiner Schlitzer) Tpot-0[°C]

Which processes create inhomogeneous DIC distribution? II. Biological C pumps



- **1. Soft tissue pump**: production of organic material in the surface ocean by phytoplankton (microalgae, size 2-50 μ m), transport (export) to deeper layers in the form of algal aggregates or faecal pellets and remineralisation (oxidation, release of CO₂) at depth by zooplankton and bacteria.
- Calcium carbonate (CaCO₃) pump: production of CaCO₃ by coccolithophores (calcifiying microalgae), foraminifera (protozoa), pteropods (marine snails, 'butterflies of the sea'), export and dissolution at depth (release of DIC) or accumulation in sediments.

The biological pumps are complex and difficult to describe quantitatively (geochemists would be happy if one could ignore 'biology'). However, 75% of the vertical DIC gradient is due to the biological pumps.



The carbon pumps







Biological C pumps: some of the key players!

Coscinodiscus oculus-iridis (diatom)

Emiliania huxleyi (coccolithophore)



... and many more

Limacina retroversa australis (pteropod, ca. 2 mm),

foraminifera



Fragilariopsis kergulensis (diatom)

Which processes create inhomogeneous DIC distribution? Great ocean conveyor belt



Biological C pumps ⇒ DIC at depth increases along the conveyor belt from the Atlantic to the Pacific

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IPCC

INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE



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total phosphate = $TPO_4 = [H_3PO_4] + [H_2PO_4] + [HPO_4^2] + [PO_4^3]$

- [Cl⁻] - [Br⁻] - [NO₃⁻] - ... $-TPO_4 + TNH_3 - 2TSO_4$

TA = $[HCO_3^{-}] + 2 [CO_3^{2-}] + [B(OH)^{-}] + [OH^{-}] - [H^{+}] + minor components$

TA \approx proton acceptors - proton donors

 $= [Na^{+}] + 2 [Mg^{2+}] + 2 [Ca^{2+}] + 2 [Sr^{2+}] + ...$





CO_2 as a function of DIC & TA





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CO_2 sequestration in the ocean



Stimulate soft tissue pump by adding nutrients: ocean iron fertilization, pump nutrients from depth into the surface layer (pipes)

Reduce CaCO₃ pump: small potential

Increase physical/solubility pump: not feasible

Increase total alkalinity: artificially enhanced weathering



CO_2 sequestration in the ocean: II Ocean Iron Fertilization (OIF)





John Martin



High Nutrient (NO₃, PO₄) Low Chlorophyll (HNLC) regions



Northern North Pacific

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Equatorial Pacific

Southern Ocean



Iron in enzymes photosystem I & II



Shi et al., 2007



Potential for Fe fertilization in the Southern Ocean? Circulation & NO₃

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AAIW Antarctic Intermediate Water SAMW = Subantarctic Mode Water

Potential for Fe fertilization in the Southern Ocean?

Macronutrients (NO₃, PO₄) leave the Southern Ocean via Antarctic Intermediate Water (AAIW) and mode waters without taking C along. Add Fe south of the AAIW/mode water formation regions to stimulate biological production and export of carbon from the surface layer.

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Potential = water transport (m³ yr⁻¹) x NO₃ concentration (mol m⁻³) x conversion to C (mol C (mol N)⁻¹) x conversion to mass (g C (mol C)⁻¹) = **1.3 Pg C yr⁻¹**

34 Sv = 34 x
$$10^6$$
 m³ s⁻¹ (Rintoul & Sloyan, 2001)

 $NO_3 = 15 \ \mu mol \ L^{-1}$

Sarmiento & Orr (1991): Complete macronutrient depletion due to iron fertilization of HNLC regions \Rightarrow 98 - 181 Pg C over 100 years \Rightarrow 1 - 1.8 Pg C yr⁻¹



Iron fertilization experiments







LOHAFEX = LOHA (iron, Hindi) Fertilization

7 January - 17 March 2009





Political storm



The Times



action group on erosion, technology and concentration

January 7, 2009

Sigmar Gabriel, MdB z.H. Sören Heinze Platz der Republik 1 11011 Berlin



- -> write risk assessment evaluated by British Antarctic Survey, IfM-GEOMAR Kiel
- & reviews by legal advisers

Close Window

Rogue ship sails into storm over experiment

Bobby Jordan

Published:Jan 11, 2009

Critics say dumping fertiliser into ocean to 'fix' climate change is fraught with risk

South Africa is caught up in a diplomatic row over a rogue science ship that slipped out of Cape Town harbour to conduct a controversial climate change experiment.

The ship set sail on Wednesday night in breach of a UN ban on "fertilising" the ocean — and South Africa has been asked to intercept the vessel.

The German-flagged RV Polarstern is loaded with iron sulphate it plans to dump deep in the Southern Ocean during a 70-day research experiment conducted by German and Indian scientists.

The 20-ton chemical cargo — normally used to treat lawns and sewage — is likely to provoke a massive algal bloom big enough to be seen from outer space. Scientists are hoping the algae will provide a quick fix to climate change by absorbing carbon into the sea, rather than letting it escape as gas into the earth's atmosphere.



CONTROVERSIAL MISSION: The German-flagged RV Polarstern in Cape Town harbour this week. South Africa has been asked to intercept the ship. Picture: IAN SHIFFMAN



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PRL - Geochemist Wissenschaftler ANT-XXV-3



Tom - Thomas Bresinsky Director / Cinematographer

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Perturbation experiment

... to investigate the structure and functioning of pelagic ecosystems

Pertubation:

Add 20 t of iron sulfate over an area of 300 km² \approx 4 t of iron \approx 0.01 g Fe m⁻² (4000 m water column contains about ten times more Fe)

 \Rightarrow concentration in mixed layer: 2 nmol L⁻¹

(tap or mineral waters may show 100 times higher concentrations).

Avoid too much spreading/dilution of patch (initial radius 10 km) by fertilizing centre of a mesoscale eddy (radius 60 km)





A good eddy should ...

- ... be **stable** for at least 2 months. (finite size Lyapounov exponents)
- ... contain **high nutrient concentrations** in surface layer.
- ... contain a **seed population of phytoplankton** (0.5 mg chlorophyll m⁻³ is lower limit).



-17

-16

Real-Time Mesoscale Altimetry - Jan 25, 2009

-15 -14 -13 -12



Phytoplankton: Who will win?



dinoflagellate (Ceratium) Emilinia huxleyi (coccolithophore) a



Measurements





N₂O: no change







CTD rosette (Conductivity, Temperature, Depth) *HELMHOLTZ* Underwater Video Profiler (UVP)



LOHAFEX algal bloom

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Carbon export? CO₂ uptake?



Chlorophyll increased by factor 2-3 (5 during EIFEX), mainly due to picophytoplankton.

Recycling system with considerable turnover.

 \Rightarrow Expectation: low carbon export.

Confirmed by sediment traps, particle recorder, ...

CO₂ uptake from atmosphere was low.





Iron addition stimulated production. Accumulation rates of phytoplankton increased for a very short time only because of heavy grazing pressure by zooplankton. **Picophytoplankton and zooplankton profited most**. Positive effects are expected for higher trophic levels.

LOHAFEX showed that iron fertilization of nutrient-rich (NO₃,PO₄) waters does not necessarily lead to algal blooms, carbon export and thus CO₂ uptake (it's not just chemistry: NO₃ + PO₄ + Fe \Rightarrow ...).

The state and functioning of the whole ecosystem plays an essential role; in particular: the plankton assemblage (initial conditions) and the amount of silicic acid.

⇒ Iron fertilization makes no sense here!



LOHAFEX: geoengineering or basic research?



Geoengineering: develop, optimize, and apply methods for the reduction of atmospheric greenhouse gases or reduction of incoming solar radiation in order to mitigate climate change. Observation of low C export is a failure.

Basic research: Investigate the structure and functioning of ecosystems under various conditions. Observation of low C export is a major result and not a failure.

When we came home from LOHAFEX we were exhausted & happy!



The C cycle on long time scales: weathering of silicate rock







Weathering rates depend on:



Surface to volume ratio of rock: mechanical weathering increases chemical weathering!

Temperature: reactions proceed faster in warmer climate

Precipitation: water is needed

Acidity of ground water: atmospheric CO₂ and organics have an influence



Artificially enhanced weathering of olivine HELMHOLTZ $Mg_2SiO_4 + 4 CO_2 + 4 H_2O \Rightarrow 2 Mg^{2+} + 4 HCO_3^- + H_4SiO_4$



ASSOCIATIO

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Requirements: small grain size (< 10 μ m), high temperature, low pH -> reactors or soils in tropical regions

Abstract. Weathering and subsequent precipitation of Ca- and Mg-carbonates are the main processes that control the CO₂-concentration in the atmosphere. It seems logical, therefore, to use enhanced weathering as a tool to reduce rising CO_2 -levels. This can be applied as a technology, by reacting captured CO₂ with olivine or calcium-silicates in autoclaves. It can also be applied extensively, by spreading fine-powdered olivine on farmland or forestland. Measures to control the CO₂-levels of the atmosphere will be adopted more readily if they also serve some broader economic goals. An effective strategy for CO₂ control will require many parallel approaches simultaneously.



The geoengineering potential of artificially enhanced silicate weathering of olivine

Peter Köhler,¹ Jens Hartmann,² Dieter A. Wolf-Gladrow¹

Consider olivine dissolution in catchment areas of Amazon & Congo. 1 g CO_2 sequestration \approx 1 g olivine (-> huge amounts of olivine!)

Problems:

- 1. Increase of river pH from below 7 to 8 or 9 ('river alkalinization').
- 2. Dissolution of silicic acid would limit potential to < 1 Pg C yr⁻¹.



Ocean pipes: nutrients from the deep Lovelock & Rapley (2007)



SIR — We propose a way to stimulate the Earth's capacity to cure itself, as an emergency treatment for the pathology of global warming.

Measurements of the climate system show that the Earth is fast becoming a hotter planet than anything yet experienced by humans. Processes that would normally regulate climate are being driven to amplify warming. Such feedbacks, as well as the inertia of the Earth system — and that of our response make it doubtful that any of the wellintentioned technical or social schemes for carbon dieting will restore the status quo. What is needed is a fundamental cure.

The oceans, which cover more than 70% of the Earth's surface, are a promising place to seek a regulating influence. One approach would be to use free-floating or tethered vertical pipes to increase the mixing of nutrient-rich waters below the thermocline with the relatively barren waters at the ocean surface. (We acknowledge advice from Armand Neukermans on engineering aspects of the pipes.) Water pumped up pipes — say, 100 to 200 metres long, 10 metres in diameter and with a one-way flap valve at the lower end for pumping by wave movement would fertilize algae in the surface waters and encourage them to bloom. This would pump down carbon dioxide and produce dimethyl sulphide, the precursor of nuclei that form sunlight-reflecting clouds.

Such an approach may fail, perhaps on engineering or economic grounds. And the impact on ocean acidification will need to be taken into account.

But the stakes are so high that we put forward the general concept of using the Earth system's own energy for amelioration. The removal of 500 gigatonnes of carbon dioxide from the air by human endeavour is beyond our current technological capability. If we can't 'heal the planet' directly, we may be able to help the planet heal itself.

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Ocean pipes: nutrients & DIC from the deep *HELMHOLTZ* Dutreuil, Bopp, and Tagliabue (2009)

``Unsurprisingly, we find that deploying an array of ocean pipes acts to increase atmospheric CO₂ by 1.4 ppm via a 5.1% reduction in cumulative FCO₂ [air to sea CO2 flux], despite augmenting carbon export by 5.6%. This is contrary to the expectations of Lovelock and Rapley (2007) and results from increased mixing with sub-surface DICrich waters (Table 1, as noted by Shepherd et al., 2007), which overwhelms any beneficial response due to increased export and alkalinity supply. The positive anomalies in biological productivity and carbon export are maximal over the first few years of the experiment and decay by 20–30% after 20 years of deployment (Fig. 4). We further note that if we eliminate the non-local effects and mix the entire global ocean then while carbon export is over 50% greater, atmospheric CO_2 increases by over 20 ppm. Accordingly, carbon export and FCO₂ are clearly decoupled in response to changes in ocean mixing.



Physical/solubility C pump: enhanced downwelling (Zhou & Flynn, 2005)



Abstract. Downwelling ocean currents carry carbon into the deep ocean (the solubility pump), and play a role in controlling the level of atmospheric carbon. The formation of North Atlantic Deep Water (NADW) also releases heat to the atmosphere, which is a contributor to a mild climate in Europe. One possible response to the increase in anthropogenic carbon in the atmosphere and to the possible weakening of the NADW is modification of downwelling ocean currents, by an increase in carbon concentration or volume. This study assesses the costs of seven possible methods of modifying downwelling currents, including using existing industrial techniques for exchange of heat between water and air. Increasing carbon concentration in downwelling currents is not practical due to the high degree of saturation of high latitude surface water. Two of the methods for increasing the volume of downwelling currents were found to be impractical, and four were too expensive to warrant further consideration. Formation of thicker sea ice by pumping ocean water onto the surface of ice sheets is the least expensive of the methods identified for enhancing downwelling ocean currents. Modifying downwelling ocean currents is highly unlikely to ever be a competitive method of sequestering carbon in the deep ocean, but may find future application for climate modification.







Final remarks



Large scale experiment (Revelle & Suess, 1957): anthropogenic CO₂ emissions & climate change & ocean acidification

Finish this experiment (mitigation) or adapt to the consequences or counteract/combat the effects (geoengineering)

Some geoengineering methods (iron fertilization, enhanced silicate weathering) have the potential to sequester large amount of CO_2 in the ocean (order of 1 Pg C yr⁻¹).

These methods have (not well known) impacts on marine ecosystems (general problem for CO2 sequestration in the ocean).

Geoengineering: trade-off or torture?

Sustainable development













Royal Society, London

Geoengineering the climate Science, governance and uncertainty September 2009

