Happamoittavien päästöjen vaikutus ilmakehän hiilidioksiditasapainoon.

TkT Tuomo Suntola

Termodynaaminen analyysi osoittaa, että valtameret-ilmakehä -systeemiä suljettuna systeeminä tarkasteltuna, vuotuiset rikki- ja typpioksidien päästöt valtamerten 10 metrin pintaveteen sekoitettuna rajoittavat ilmakehään syötetyn hiilidioksidin liukenemista siten, että hiilidioksidin tasapainotilaa vastaava osapaine ilmakehässä nousee havaittua 0,4 prosentin vuotuista kasvua vastaavalle tasolle.

Living with Climate Variability and Change, WMO2006, 17-21.7.2006, Espoo, Finland.
Suntola, T., Turunen, H., Kobylin, P., Salminen, J., Liukkonen, S., *Do the SOx and NOx emissions contribute to the increase of the CO2 level through acidification of soil and waters?,*

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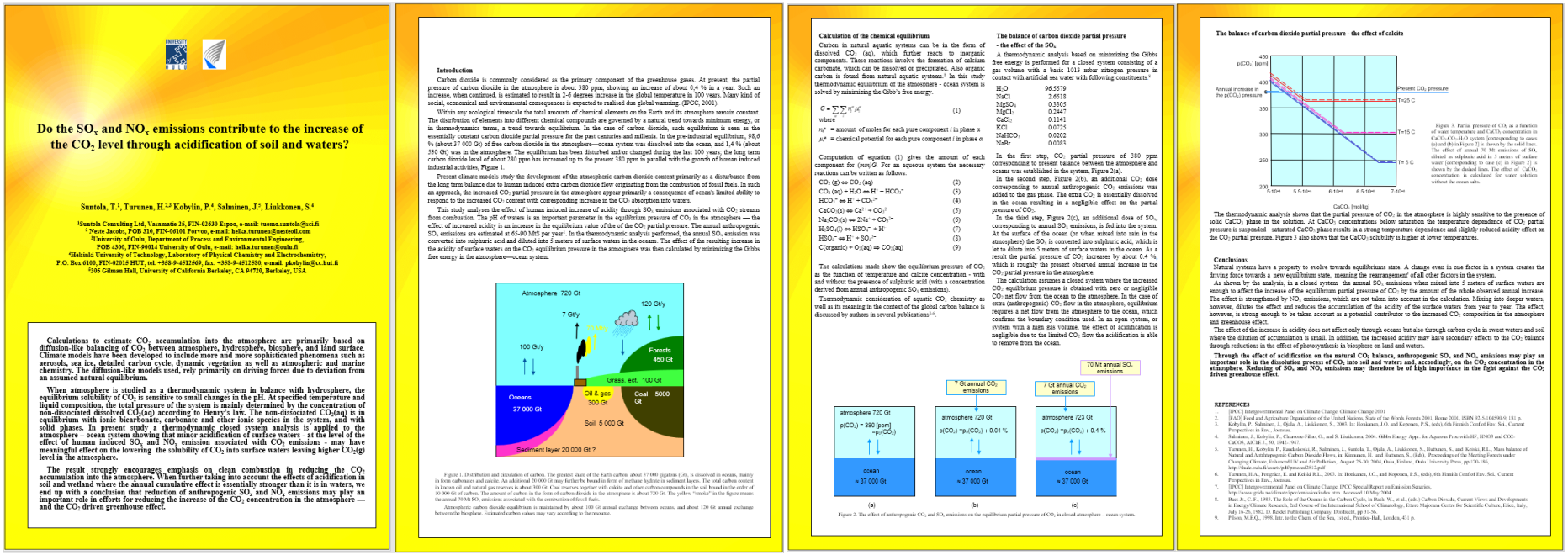

Do the SO_x and NO_x emissions contribute to the increase of the CO_2 level through acidification of soil and waters?

Suntola, T.[1], Turunen, H.[2,3] Kobylin, P.[4], Salminen, J.[2], Liukkonen, S.[4]

[1]Suntola Consulting Ltd, Vasamatie 26, FIN-02630 Espoo, e-mail: tuomo.suntola@sci.fi
[2] Neste Jacobi, POB 310, FIN-06101 Porvoo, e-mail: heiki.turunen@nestoil.com
[3]University of Oulu, Department of Process and Environmental Engineering, POB 4300, FIN-90014 University of Oulu, e-mail: heiki.turunen@oulu.fi
[4]Helsinki University of Technology, Laboratory of Physical Chemistry and Electrochemistry, P.O. Box 6100, FIN-02015 HUT, tel. +358-9-4512509, fax: +358-9-4512580, e-mail: pkobylin@cc.hut.fi
[5]305 Gilman Hall, University of California Berkeley, CA 94720, Berkeley, USA

Calculations to estimate CO_2 accumulation into the atmosphere are primarily based on diffusion-like balancing of CO_2 between atmosphere, hydrosphere, biosphere, and land surface. Climate models have been developed to include more and more sophisticated phenomena such as aerosols, sea ice, detailed carbon cycle, dynamic vegetation as well as atmospheric and marine chemistry. The diffusion-like models used, rely primarily on driving forces due to deviation from an assumed natural equilibrium.

When atmosphere is studied as a thermodynamic system in balance with hydrosphere, the equilibrium solubility of CO_2 is sensitive to small changes in the pH. At specified temperature and liquid composition, the total pressure of the system is mainly determined by the concentration of non-dissociated dissolved CO_2(aq) according to Henry's law. The non-dissociated CO_2(aq) is in equilibrium with ionic bicarbonate, carbonate and other ionic species in the system, and with solid phases. In present study a thermodynamic closed system analysis is applied to the atmosphere – ocean system showing that minor acidification of surface waters - at the level of the effect of human induced SO_x and NO_x emission associated with CO_2 emissions - may have meaningful effect on the lowering the solubility of CO_2 into surface waters leaving higher CO_2(g) level in the atmosphere.

The result strongly encourages emphasis on clean combustion in reducing the CO_2 accumulation into the atmosphere. When further taking into account the effects of acidification in soil and wetland where the annual cumulative effect is essentially stronger than it is in waters, we end up with a conclusion that reduction of anthropogenic SO_x and NO_x emissions may play an important role in efforts for reducing the increase of the CO_2 concentration in the atmosphere — and the CO_2 driven greenhouse effect.

Introduction

Carbon dioxide is commonly considered as the primary component of the greenhouse gases. At present, the partial pressure of carbon dioxide in the atmosphere is about 380 ppm, showing an increase of about 0.4 % in a year. Such an increase, when continued, is estimated to result in 2–6 degrees increase in the global temperature in 100 years. Many kind of social, economical and environmental consequences is expected to realised due global warming. (IPCC, 2001).

Within any ecological timescale the total amounts of chemical elements on the Earth and its atmosphere remain constant. The distribution of elements into different chemical compounds are governed by a natural trend towards minimum energy, or in thermodynamics terms, a trend towards equilibrium. In the case of carbon dioxide, such equilibrium is seen as the essentially constant carbon dioxide partial pressure for the past centuries and millenia. In the pre-industrial equilibrium, 95.6 % (about 37 000 Gt) of free carbon dioxide in the atmosphere—ocean system was dissolved into the ocean, and 1.4 % (about 530 Gt) was in the atmosphere. The equilibrium has been disturbed and/or changed during the last 100 years; the long term carbon dioxide level of about 280 ppm has increased up to the present 380 ppm in parallel with the growth of human induced industrial activities, Figure 1.

Present climate models study the development of the atmospheric carbon dioxide content primarily as a disturbance from the long term balance due to human induced extra carbon dioxide flow originating from the combustion of fossil fuels. In such an approach, the increased CO_2 partial pressure in the atmosphere appear primarily a consequence of ocean's limited ability to respond to the increased CO_2 content with corresponding increase in the CO_2 absorption into waters.

This study analyses the effect of human induced increase of acidity through SO_x emissions associated with CO_2 streams from combustion. The pH of waters is an important parameter in the equilibrium pressure of CO_2 in the atmosphere — the effect of increased acidity is an increase in the equilibrium value of the of the CO_2 partial pressure. The annual anthropogenic SO_x emissions are estimated at 65-90 MtS per year. In the thermodynamic analysis performed, the annual SO_x emission was converted into sulphuric acid and diluted into 5 meters of surface waters in the oceans. The effect of the resulting increase in the acidity of surface waters on the CO_2 equilibrium pressure in the atmosphere was then calculated by minimizing the Gibbs free energy in the atmosphere—ocean system.

Figure 1. Distribution and circulation of carbon. The greatest share of the Earth carbon, about 37 000 gigatons (Gt), is dissolved in oceans, mainly in form carbonates and calcite. An additional 20 000 Gt may further be bound in form of methane hydrate in sediment layers. The total carbon content in known oil and natural gas reserves is about 300 Gt. Coal reserves together with calcite and other carbon compounds in the soil bound in the order of 10 000 Gt of carbon. The amount of carbon in the form of carbon dioxide in the atmosphere is about 720 Gt. The yellow "smoke" in the figure means the annual 70 Mt SO_x emissions associated with the combustion of fossil fuels.

Atmospheric carbon dioxide equilibrium is maintained by about 100 Gt annual exchange between oceans, and about 120 Gt annual exchange between the biosphere. Estimated carbon values may vary according to the resource.

Calculation of the chemical equilibrium

Carbon in natural aquatic systems can be in the form of dissolved CO_2 (aq), which further reacts to inorganic components. These reactions involve the formation of calcium carbonate, which can be dissolved or precipitated. Also organic carbon is found from natural aquatic systems.[1] In this study thermodynamic equilibrium of the atmosphere - ocean system is solved by minimizing the Gibb's free energy.

$$G = \sum_{\alpha} \sum_{i} n_i^{\alpha} \mu_i^{\alpha} \quad (1)$$

where

n_i^{α} = amount of moles for each pure component i in phase α

μ_i^{α} = chemical potential for each pure component i in phase α

Computation of equation (1) gives the amount of each component for (min)G. For an aqueous system the necessary reactions can be written as follows:

$$CO_2(g) \Leftrightarrow CO_2(aq) \quad (2)$$
$$CO_2(aq) + H_2O \Leftrightarrow H^+ + HCO_3^- \quad (3)$$
$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad (4)$$
$$CaCO_3(s) \Leftrightarrow Ca^{2+} + CO_3^{2-} \quad (5)$$
$$Na_2CO_3(s) \Leftrightarrow 2Na^+ + CO_3^{2-} \quad (6)$$
$$H_2SO_4(l) \Leftrightarrow HSO_4^- + H^+ \quad (7)$$
$$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-} \quad (8)$$
$$C(organic) + O_2(aq) \Leftrightarrow CO_2(aq) \quad (9)$$

The calculations made show the equilibrium pressure of CO_2 as the function of temperature and calcite concentration - with and without the presence of sulphuric acid (with a concentration derived from annual anthropogenic SO_x emissions).

Thermodynamic consideration of aquatic CO_2 chemistry as well as its meaning in the context of the global carbon balance is discussed by authors in several publications[1-6].

The balance of carbon dioxide partial pressure - the effect of the SO_x

A thermodynamic analysis based on minimizing the Gibbs free energy is performed for a closed system consisting of a gas volume with a basic 1013 mbar nitrogen pressure in contact with artificial sea water with following constituents.[7]

H_2O	96.5579
NaCl	2.6518
$MgSO_4$	0.3305
$MgCl_2$	0.2447
$CaCl_2$	0.1141
KCl	0.0725
$NaHCO_3$	0.0202
NaBr	0.0083

In the first step, CO_2 partial pressure of 380 ppm corresponding to present balance between the atmosphere and oceans was established in the system, Figure 2(a).

In the second step, Figure 2(b), an additional CO_2 dose corresponding to annual anthropogenic CO_2 emissions was added to the gas phase. The extra CO_2 is essentially dissolved in the ocean resulting in a negligible effect on the partial pressure of CO_2.

In the third step, Figure 2(c), an additional dose of SO_x, corresponding to annual SO_x emissions, is fed into the system. At the surface of the ocean (or when mixed into rain in the atmosphere) the SO_x is converted into sulphuric acid, which is let to dilute into 5 meters of surface waters in the ocean. As a result the partial pressure of CO_2 increases by about 0.4 %, which is roughly the present observed annual increase in the CO_2 partial pressure in the atmosphere.

The calculation assumes a closed system where the increased CO_2 equilibrium pressure is obtained with zero or negligible CO_2 net flow from the ocean to the atmosphere. In the case of extra (anthropogenic) CO_2 flow in the atmosphere, equilibrium requires a net flow from the atmosphere to the ocean, which confirms the boundary condition used. In an open system, or system with a high gas volume, the effect of acidification is negligible due to the limited CO_2 flow the acidification is able to remove from the ocean.

Figure 2. The effect of anthropogenic CO_2 and SO_x emissions on the equilibrium partial pressure of CO_2 in closed atmosphere – ocean system.

The balance of carbon dioxide partial pressure - the effect of calcite

Figure 3. Partial pressure of CO_2 as a function of water temperature and $CaCO_3$ concentration in $CaCO_3$-CO_2-H_2O system (corresponding to cases (a) and (b) in Figure 2) is shown by the solid lines. The effect of annual 70 Mt emissions of SO_x diluted as sulphuric acid in 5 meters of surface water (corresponding to case (c) in Figure 2) is shown by the dashed lines. The effect of $CaCO_3$ concentration is calculated for water solution without the ocean salts.

The thermodynamic analysis shows that the partial pressure of CO_2 in the atmosphere is highly sensitive to the presence of solid $CaCO_3$ phase in the solution. At $CaCO_3$ concentrations below saturation the temperature dependence of CO_2 partial pressure is suspended - saturated $CaCO_3$ phase results in a strong temperature dependence and slightly reduced acidity effect on the CO_2 partial pressure. Figure 3 also shows that the $CaCO_3$ solubility is higher at lower temperatures.

Conclusions

Natural systems have a property to evolve towards equilibriums state. A change even in one factor in a system creates the driving force towards a new equilibrium state, meaning the 'rearrangement' of all other factors in the system.

As shown by the analysis, in a closed system the annual SO_x emissions when mixed into 5 meters of surface waters are enough to affect the increase of the equilibrium partial pressure of CO_2 by the amount of the whole observed annual increase. The effect is strengthened by NO_x emissions, which are not taken into account in the calculation. Mixing into deeper waters, however, dilutes the effect and reduces the accumulation of the acidity of the surface waters from year to year. The effect, however, is strong enough to be taken account as a potential contributor to the increased CO_2 composition in the atmosphere and greenhouse effect.

The effect of the increase in acidity does not affect only through oceans but also through carbon cycle in sweet waters and soil where the dilution of accumulation is small. In addition, the increased acidity may have secondary effects to the CO_2 balance through reductions in the effect of photosynthesis in biosphere on land and waters.

Through the effect of acidification on the natural CO_2 balance, anthropogenic SO_x and NO_x emissions may play an important role in the dissolution process of CO_2 into soil and waters and, accordingly, on the CO_2 concentration in the atmosphere. Reducing of SO_x and NO_x emissions may therefore be of high importance in the fight against the CO_2 driven greenhouse effect.

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IPCC Special Report

Carbon Dioxide Capture and Storage

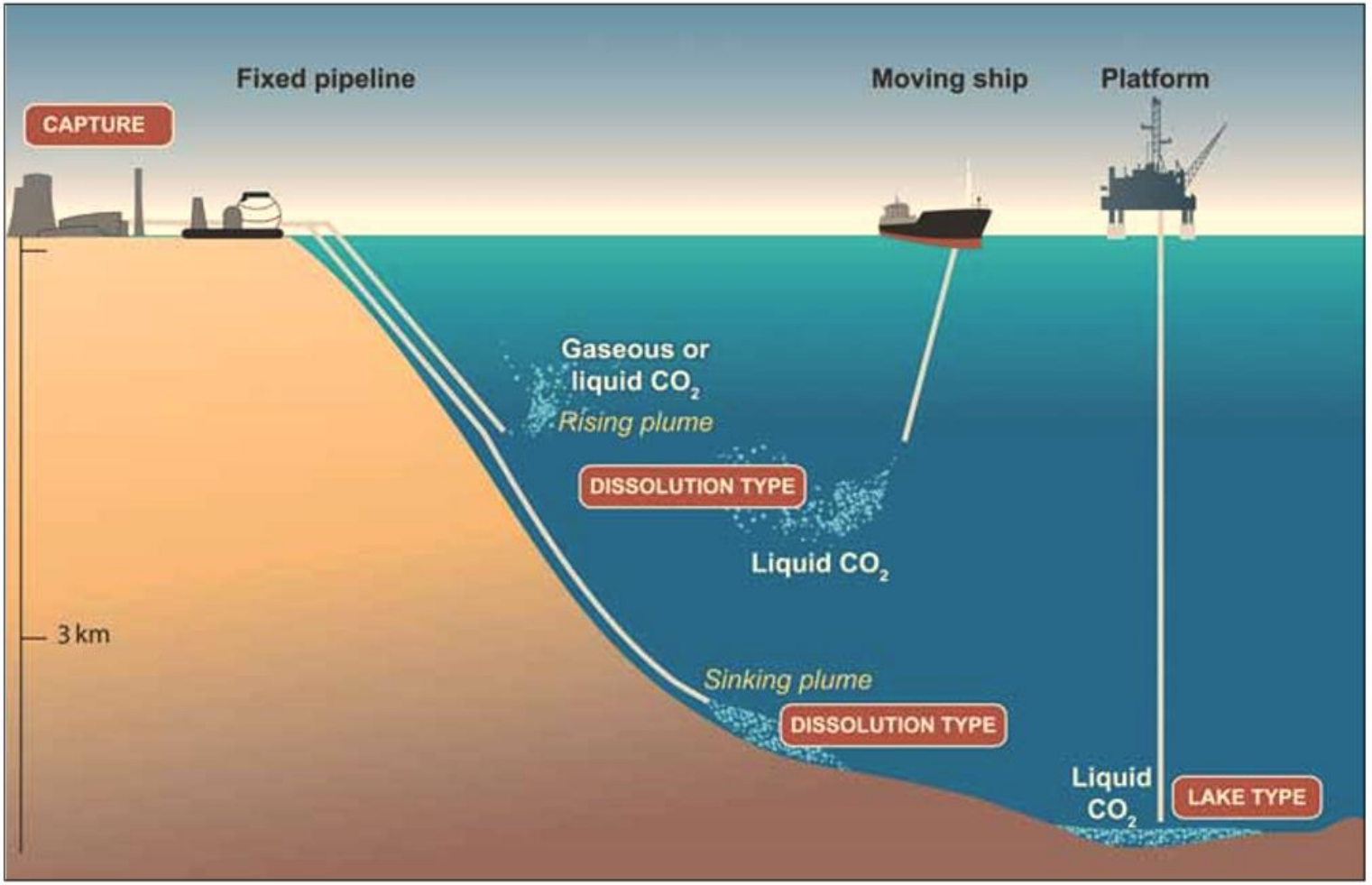

Figure SPM.5. Overview of ocean storage concepts. In "dissolution type" ocean storage, the CO_2 rapidly dissolves in the ocean water, whereas in "lake type" ocean storage, the CO_2 is initially a liquid on the sea floor (Courtesy CO2CRC).

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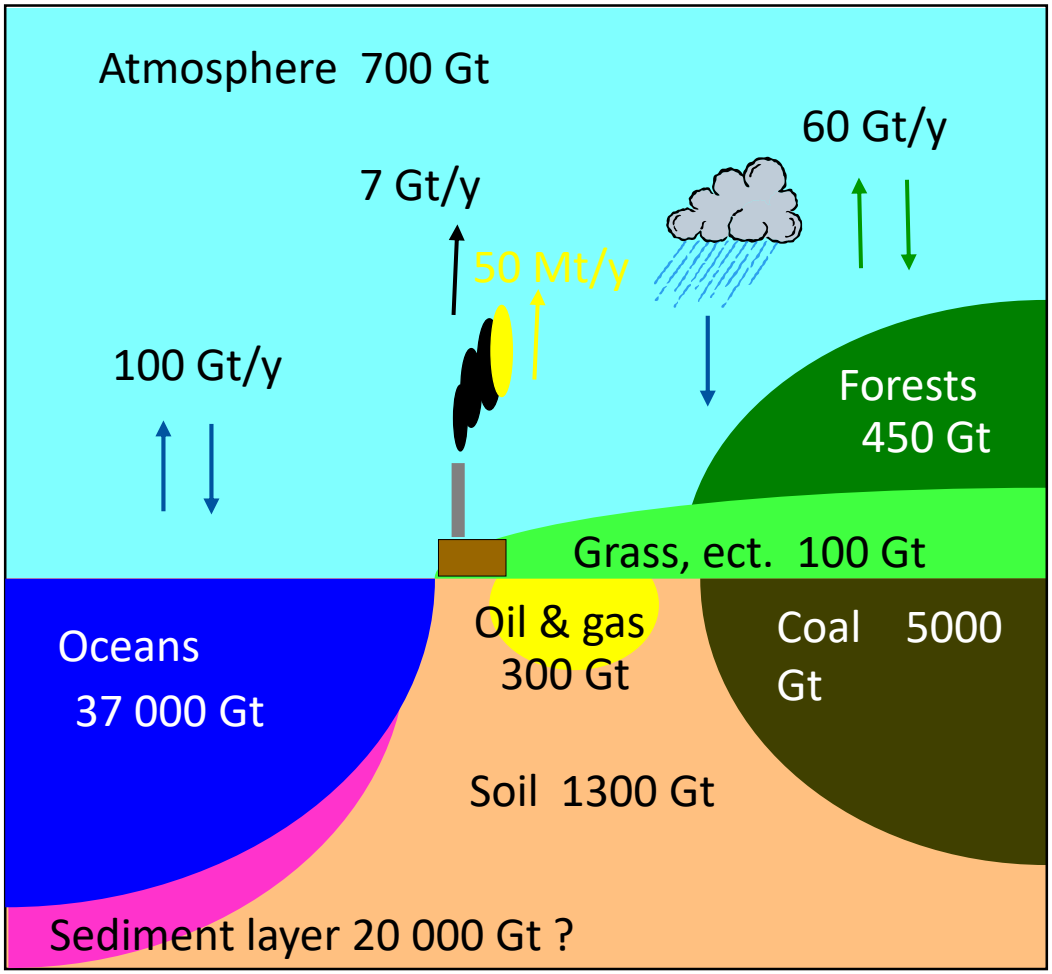
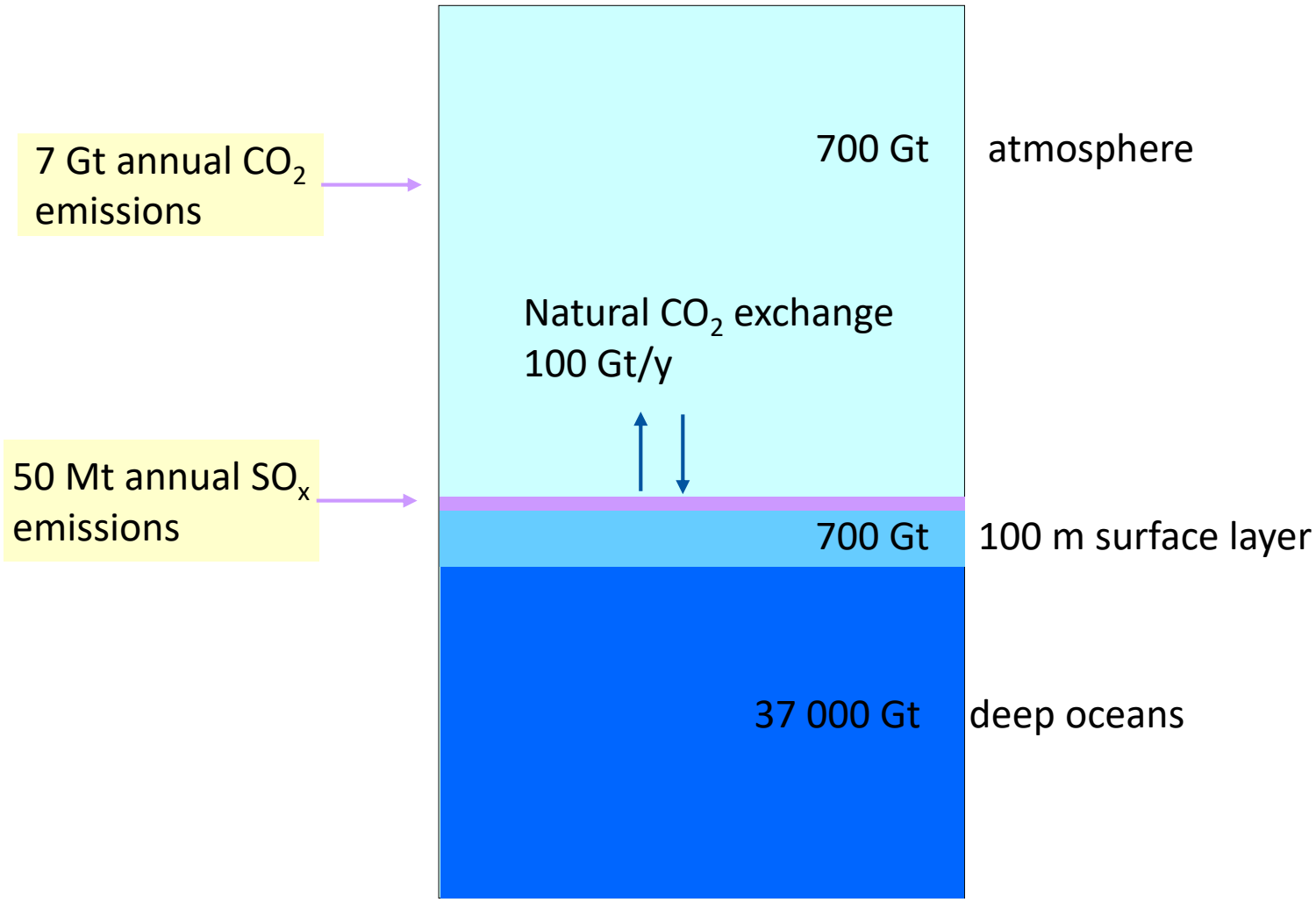
Carbon circulation in nature



Sedimentary rocks (limestone) 70 000 000 Gt ?

Carbon distribution in atmosphere and oceans



Reaction equations and the calculation procedure for the multiphase $CaCO_3$-CO_2-H_2O system in the presence of sulfuric acid

$$CO_2(g) \Leftrightarrow CO_2(aq) \quad (1)$$

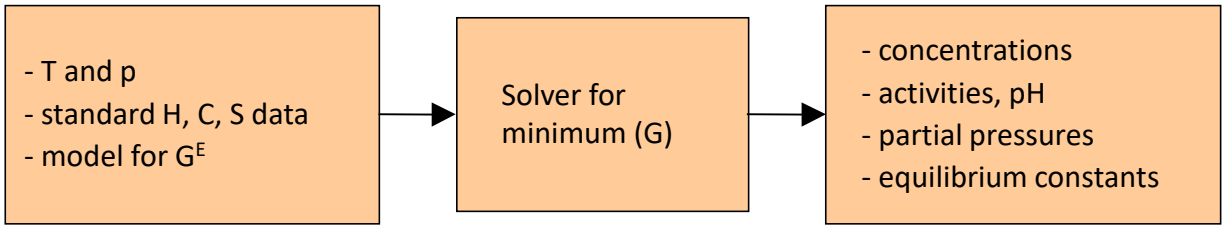
$$CO_2(aq) + H_2O \Leftrightarrow H^+ + HCO_3^- \quad (2)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad (3)$$

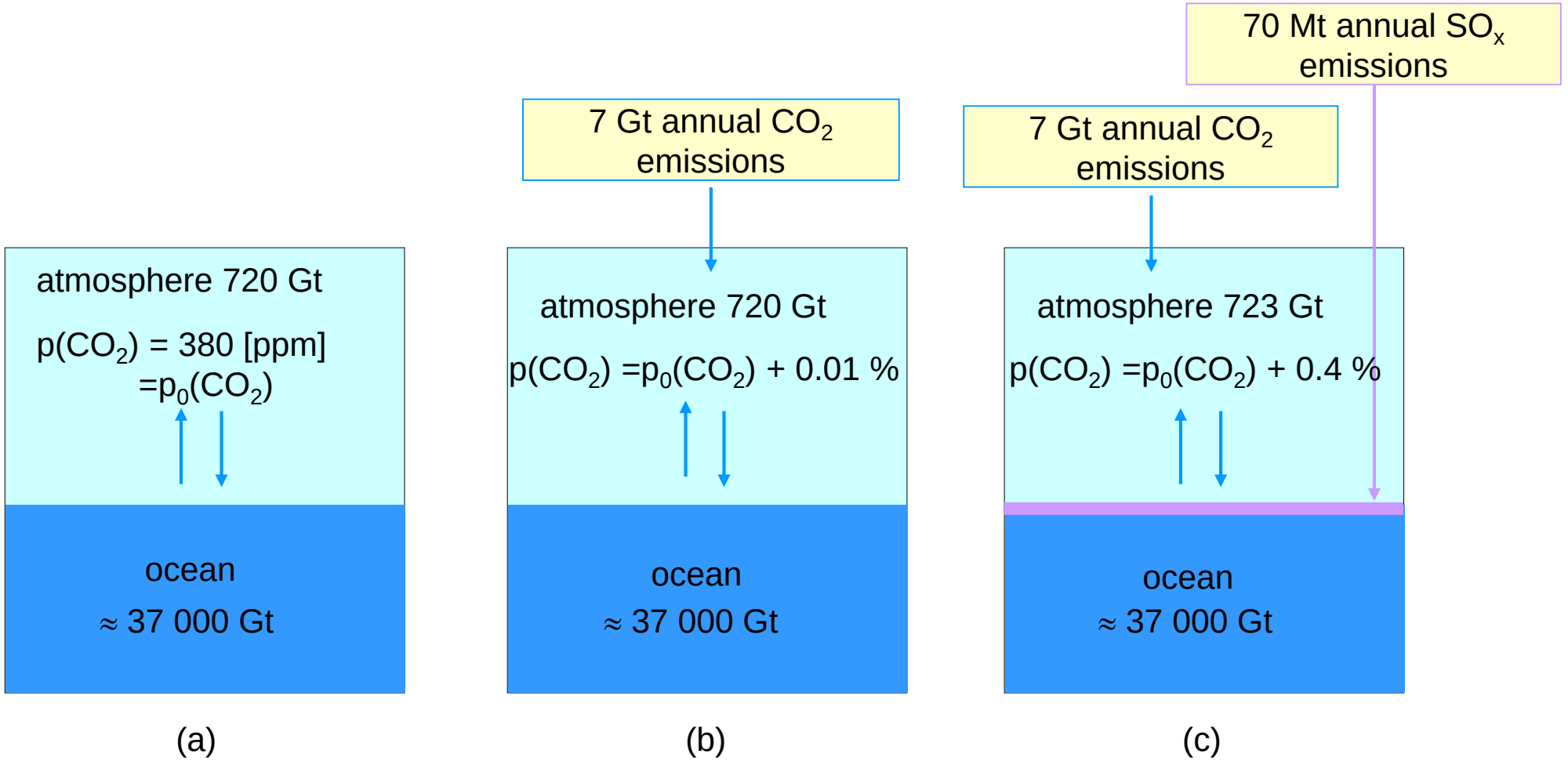
$$CaCO_3(s) \Leftrightarrow Ca^{2+} + CO_3^{2-} \quad (4)$$

$$H_2SO_4(l) \Leftrightarrow HSO_4^- + H^+ \quad (5)$$

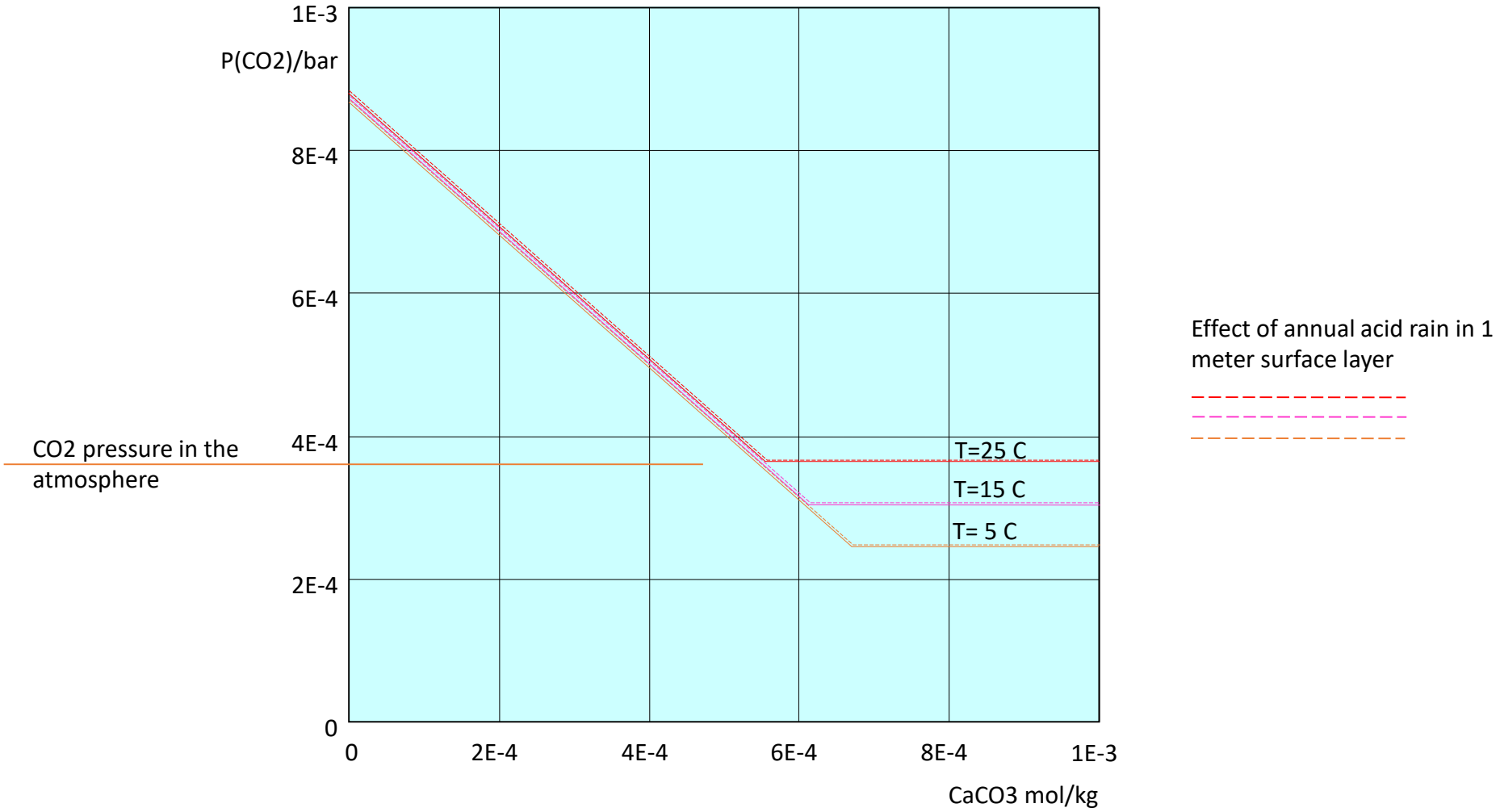
$$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-} \quad (6)$$



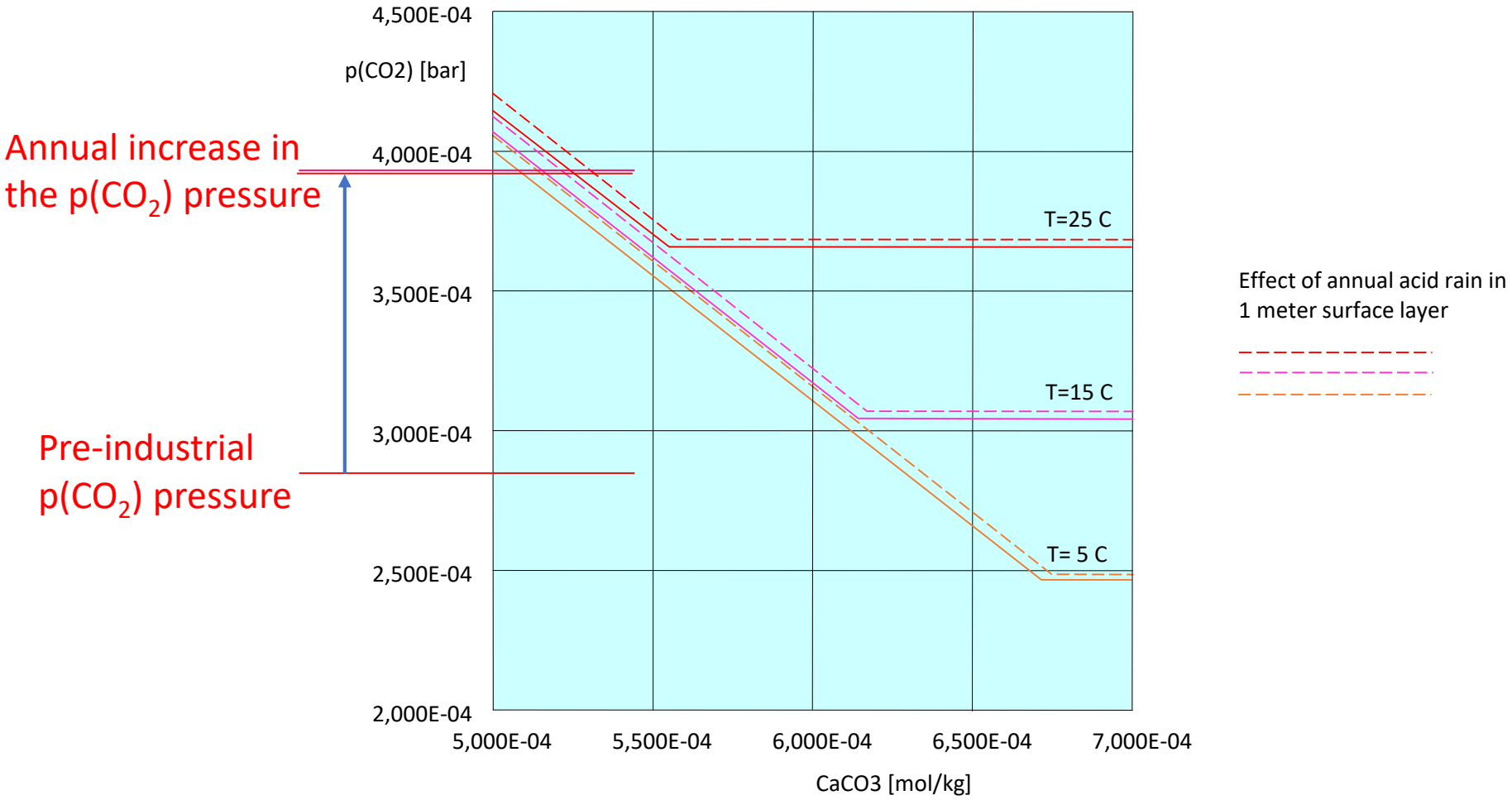
The effect of anthropogenic CO_2 and SO_x emissions on the equilibrium partial pressure of CO_2 in closed atmosphere – ocean system.



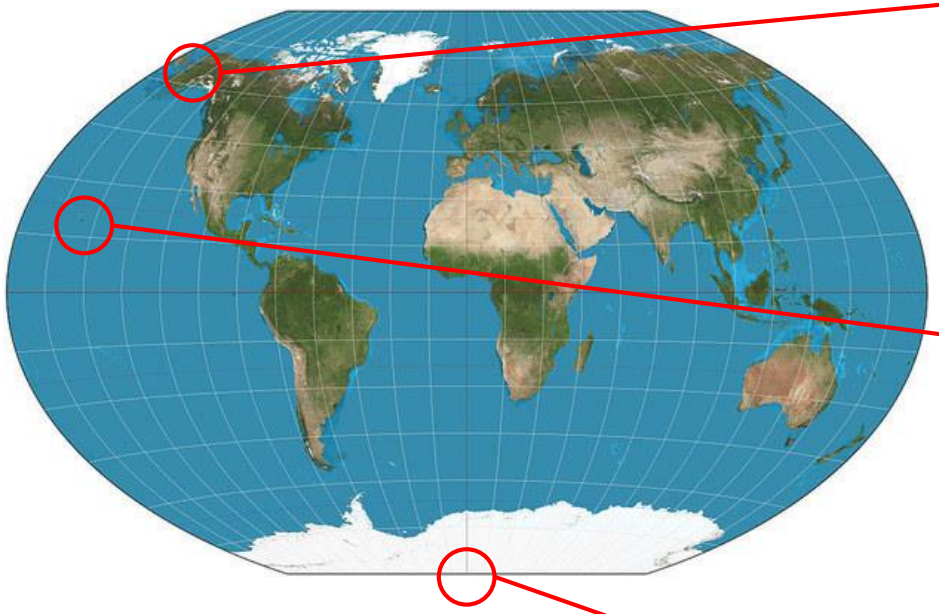
Equilibrium between CO_2 pressure and ocean at different temperatures

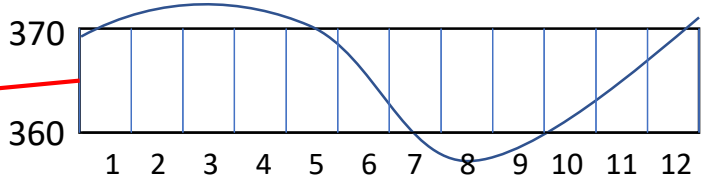


Equilibrium between CO_2 pressure and ocean at different temperatures

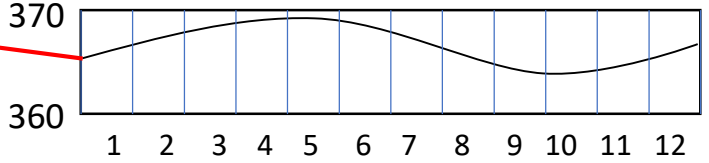


Annual variation of atmospheric CO_2 pressure

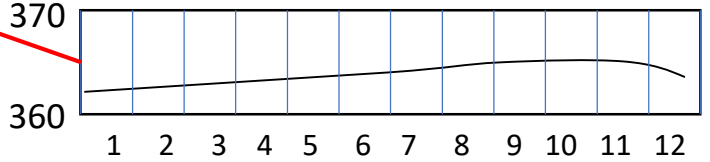




Alaska



Mauna Loa

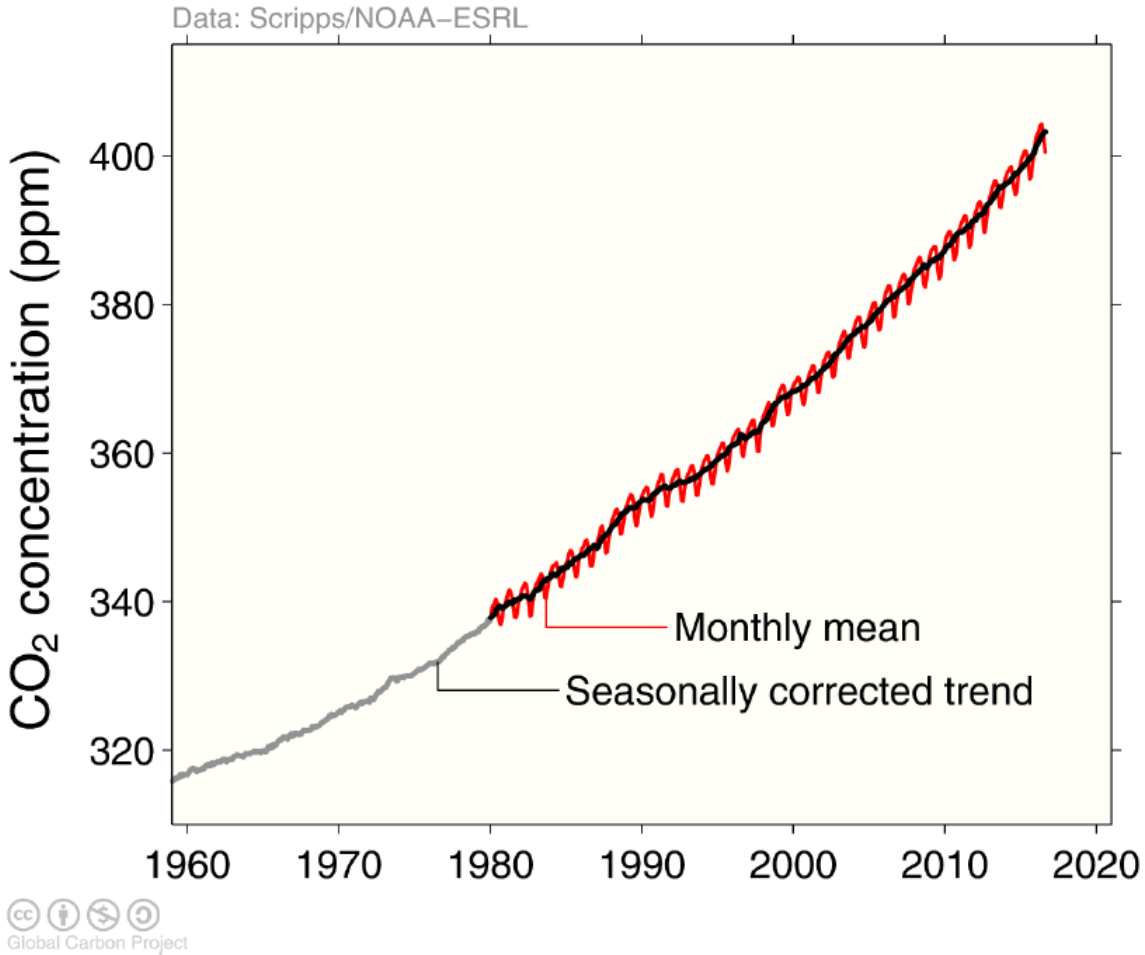


South Pole

Atmospheric concentration

The global CO_2 concentration increased from ~277ppm in 1750 to 399ppm in 2015 (up 44%)

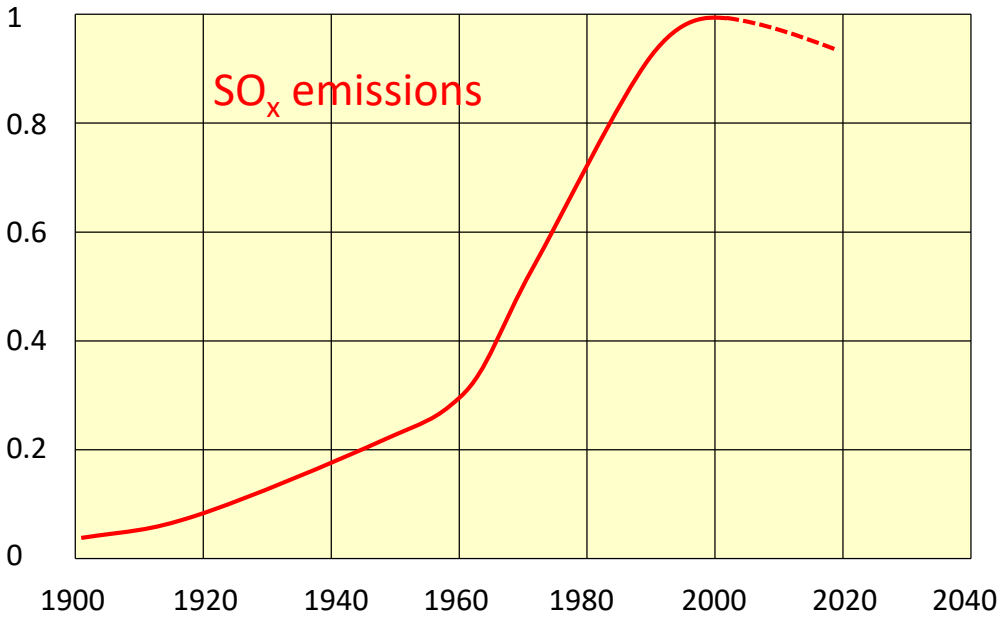
2016 will be the first full year with concentration above 400ppm



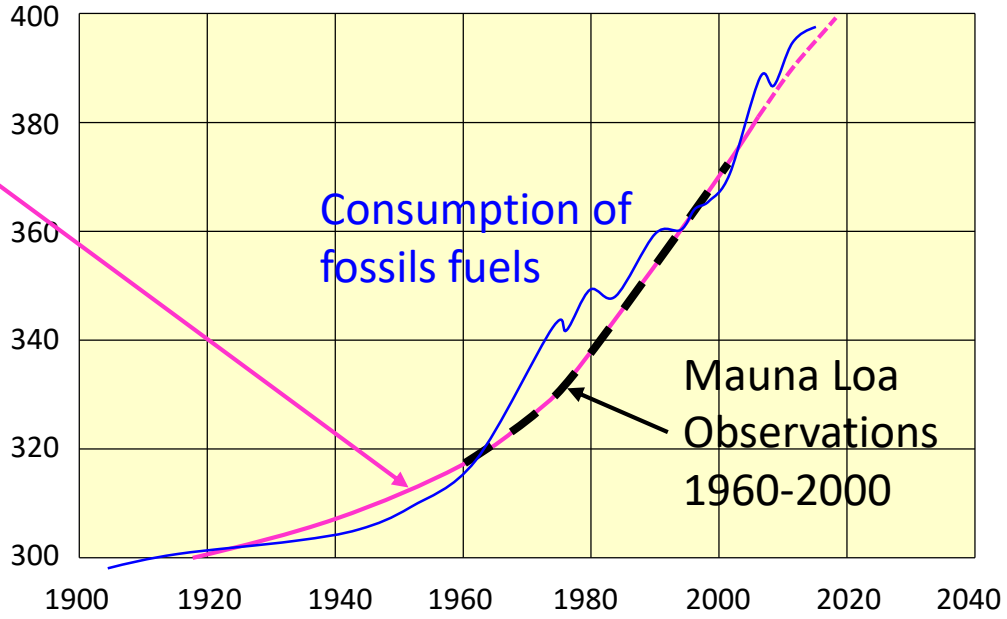
Globally averaged surface atmospheric CO_2 concentration. Data from: NOAA-ESRL after 1980; the Scripps Institution of Oceanography before 1980 (harmonised to recent data by adding 0.542ppm)

Source: NOAA-ESRL; Scripps Institution of Oceanography; Le Quéré et al 2016; Global Carbon Budget 2016

Effect of SO_x emissions on atmospheric CO_2 equilibrium



Calculated effect of SO_x emissions on CO_2 pressure by 3,9 m effective surface layer



Global Warming & Climate Change

IPCC: The average global temperature is rising sharply due to increasing concentrations of greenhouse gases (GHGs) in the atmosphere.

"Humans are contributing to the greenhouse effect by emitting greenhouse gases (GHGs) that trap energy and warm the atmosphere. Most of the emissions come from burning fossil fuels such as coal, oil and gasoline."

… OR …

Humans are contributing to the greenhouse effect by disturbing the balance of carbon dioxide between the atmosphere, soil and waters.

Global Warming & Climate Change

"Humans are contributing to the greenhouse effect by disturbing the balance of carbon dioxide between the atmosphere, soil and waters."

Through the effect of acidification on the natural CO_2 balance, anthropogenic SO_x and NO_x emissions may play an important role in the dissolution process of CO_2 into soil and waters and, accordingly, on the CO_2 concentration in the atmosphere. Reducing of SO_x and NO_x emissions may therefore be of high importance in the fight against the CO_2 driven greenhouse effect.