



Anthropogenic Carbon Dioxide (CO₂) Amounts and Fluxes between the Atmosphere, the Ocean, and the Biosphere

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

The author has developed one dimensional semi-empirical atmosphere-ocean-biosphere model (1DAOBM) based on the four-box presentation. Firstly, the author has analysed that the model development can be based on the two elements: 1) the four box-model containing two ideal mixing components (the atmosphere and the ocean), one plug flow component with four different residence times (the biosphere), and the outlet (the intermediate & deep ocean), 2) the ocean's capacity to dissolve anthropogenic CO₂ emissions of the present century. The surface ocean part is based on the known dissolution chemical equations. The net flux rate from the surface ocean into the deep ocean is based on the empirical data. The removal of the anthropogenic CO₂ from the atmosphere is based on the huge carbon cycle flux rates of the dissolution pump and the biosphere carbon cycle, which remove yearly about 26% of CO₂ from the atmosphere to other reservoirs and, at the same time, recycle back natural and anthropogenic carbon. The simulations of the atmospheric net CO₂ rate by 1DAOBM from 1960 to 2013 show fairly good similarity to the measured values: $r_2 = 0.75$ and the standard error of estimate 0.68 GtC/y, which means the standard error of 12% at the present emission rate of about 10 GtC/y. The simulations show that the present anthropogenic CO₂ fraction in the atmosphere is 7.7%, and it explains the observed

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$\delta^{13}\text{C}$ value of -8.4‰ extremely well. Also, the reduction of $\delta^{13}\text{C}$ in the ocean from 1900 to 2013, simulated to be -0.6‰ , is close to the observed values. The 1DAOBM has been used also to simulate the fluxes and CO_2 concentration trends corresponding to the projection RCP4.5 of IPCC. These results deviate from the IPCC's results in the descending phase of the CO_2 emissions. The mean residence time of the total atmospheric CO_2 concentration change is 32 years and that of the anthropogenic CO_2 change is 15 years, according to 1DAOBM simulations.

Keywords: Global warming; atmosphere-ocean-biosphere model; CO_2 ocean sink; biosphere sink; atmospheric anthropogenic CO_2 and $\delta^{13}\text{C}$; ocean uptake.

1. INTRODUCTION

The objectives of this paper are to show that a simple semi-empirical atmosphere-ocean-biosphere model 1) can represent the overall uptake CO_2 rate of the ocean and the biosphere, 2) can explain that the annual fluctuations of the ocean uptake CO_2 flux rates depend on the atmospheric CO_2 concentration fluctuations and on the annual surface ocean temperature fluctuations, 3) can explain that the annual fluctuations in the atmospheric CO_2 amount depend mainly on the ocean uptake changes, 4) the carbon cycle between the atmosphere, the ocean and the biosphere can explain the present anthropogenic CO_2 fraction and ^{13}C proportion in the atmosphere and in the ocean.

Table 1 includes all the symbols, abbreviations, acronyms and definitions used repeatedly in this paper.

The numerical values of the major reservoirs and fluxes of global carbon cycle vary in broad limits. A simple presentation of carbon cycle of the present time is depicted in Fig. 1.

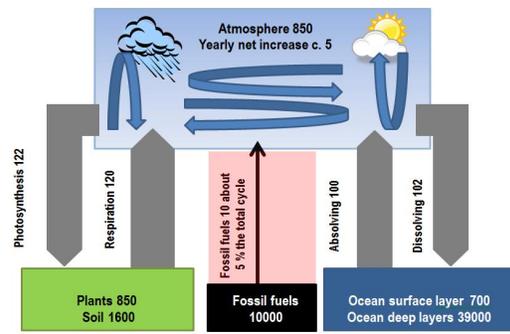


Fig. 1. A simple carbon cycle presentation. The reservoirs are in Giga tons of carbon (GtC=PgC) and fluxes in GtC/y

Table 1. List of symbols, abbreviations, and acronyms

Acronym	Definition
1DAOBM	One dimensional atmosphere-ocean-biosphere model
AR	Assessment report of IPCC
CIA	Carbon in the atmosphere
CIB	Carbon in the biosphere
CSO	Carbon in the surface ocean (mixing layer carbon)
CDO	Carbon in the deep ocean
DIC	Dissolved inorganic carbon in the ocean
DOC	Dissolved organic carbon in the ocean
F_{ff}	Emission CO_2 flux of fossil fuel combustion
F_{deep}	Anthropogenic CO_2 flux into the deep ocean
FB	Biosphere carbon cycle flux
FO	Dissolution carbon pump flux
FLUSH-%	Flush-% of a carbon pump
GCAM	Global change assessment model
IPCC	Intergovernmental panel on climate change
POC	Particulate organic carbon
$\delta^{13}\text{C}$	A unit of measure of ^{13}C isotope

Subscript_{down} means downwards, subscript_{up} means upwards, and subscript_{tot} means total, subscript_{ant} means anthropogenic, subscript_A means the atmosphere, subscript_O means the ocean, subscript_B means the biosphere, subscript_n means year n.

The values in Fig. 1 are based on the average values of four studies [1-4]. In these studies the flux values vary in the limits (GtC/y): absorbing rate 80.0 – 102, dissolving rate 78.4 – 100, photosynthesis rate 62.1 – 123, and respiration rate 61.3 – 120. The areas of the flux arrows are in relationships to the area of the atmospheric carbon reservoir. The sizes of reservoirs in Fig. 1 are based on the present situation or on the latest estimates. The broad limits in the flux values mean that the knowledge about the carbon cycle is still uncertain and limited.

The flux values in Fig. 1 mean that about 26 percent of the atmospheric CO₂ is changed yearly. According to a survey [5] consisting of 34 residence time (also called a lifetime or a turnover time) studies applying six different methods, the average value is 7.6 years and the median value is 7.5 years among the results from 2 to 15 years. The atmosphere, up to the tropopause, is close to a perfect mixing chamber, because the concentrations of different gases are almost evenly distributed including CO₂. The step response of a mixing chamber is a first order transfer function and its equation is

$$\text{Out}(t) = 1 - e^{-t/\tau}, \quad (1)$$

where Out(t) is the step response of the unit the step input, t is time and τ is the time constant calculated based on the incoming carbon flux rates into the atmosphere (850 Gt / (120 Gt/y + 100 Gt/y) = 3.9 years). This theoretical equation shows that a step change has passed through the atmosphere at the rate of 63% after 3.9 years, 86% after 7.6 years, and 93% after 10 years. The output of an ideal mixing chamber never reaches the 100% value of an input, and therefore usually a practical solution is that the time constant τ is used as a mean residence time. Because the actual situation is more complicated due to the recycling fluxes, the real residence time could be longer as found in the several studies [5]. If the mean residence time of an ideal mixer is measured, it has a long tail caused by the large distribution of the residence time. These are probably the main reasons why the studies applying different observational methods produce a certain spread in results.

IPCC [6] used in AR4 a special formula, which gives a step response giving 82% change after 100 years. In the latest report AR5 IPCC [2] does not give any specific lifetime for CO₂ but connects this issue to the recycling of the atmospheric CO₂ between the reservoirs of

ocean and land. As an example about the CO₂ lifetime, IPCC [2] informs that “after 2000 years, the atmosphere will still contain between 15% and 40% of those initial CO₂ emissions.” This result is in conflict with the big majority of other CO₂ residence time studies and the observed mixing capability of the atmosphere.

There are some studies of the atmospheric anthropogenic CO₂ residence times based on the real measurements. In the reference [7], the anthropogenic CO₂ fraction in the atmosphere was calculated based on the radioactive ¹⁴C isotope data. According to this analysis, the anthropogenic CO₂ fraction would be only 1.73% in 1957, using the atmospheric CO₂ lifetime of 7 years. Based on the mass balance fluxes, isotope ratios ¹²C/¹³C data, and CO₂ lifetime of 5 years, it was calculated that in 1988 the anthropogenic part of the CO₂ in the atmosphere was at a maximum 4% [8].

IPCC's latest value [2] for the anthropogenic CO₂-percentage in the atmosphere is 28%. This huge gap with the other research results originates from the long residence time calculation method of IPCC. This situation can be analysed by comparing the real ¹³C isotope proportions in the carbon cycle elements. The measurement unit of ¹³C proportion is δ¹³C, and its calculation formula is

$$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right) * 1000 \quad (2)$$

where δ¹³C is a fraction of carbon isotope 13 expressed as (‰) (written also in forms per mil, per mill, permil, permil or permille). The value of (¹³C/¹²C)_{standard} is 0.0112372. The δ¹³C of the natural CO₂ is about -7‰ [5]. Suess noticed first that the combustion of fossil fuels decreases ¹⁴C in the atmosphere. Today, the Suess Effect has been extended to mean a concept which shifts the isotopic ratio of both ¹³C and ¹⁴C in any reservoir of the carbon cycle owing to anthropogenic activities. The typical δ¹³C values in the present time are [9]: The atmosphere - 8.2‰, the ocean -9.5...-10‰, the biosphere - 26‰, and the fossil fuels -28‰.

Even though the δ¹³C values differ seemingly quite a lot, the real ¹³C fractions are very close to each other: δ¹³C value -7‰ means 1.11585% fraction and δ¹³C value -26‰ means 1.10945% ¹³C fraction in the carbon fluid. The basic reason for the lower δ¹³C values in the atmosphere is the photosynthesis of plants, which prefer the

isotope ^{12}C . That is why the fossil fuels have almost the same value as the biosphere, because they originate from ancient plants. A striking feature of these figures is that the atmosphere's ^{13}C proportion is -8.2‰ . If the IPCC's value of 28% anthropogenic CO_2 in the atmosphere would be true, the atmosphere's $\delta^{13}\text{C}$ should be close to -12.9‰ according to equation (3)

$$\delta^{13}\text{C} = (100 - \text{PCT}_{\text{ant}})/100 * (-7.0) + (\text{PCT}_{\text{ant}}/100) * (-28) \quad (3)$$

where $\delta^{13}\text{C}$ is the ^{13}C fraction in the atmosphere holding PCT_{ant} anthropogenic CO_2 percentage. Because this is not the case, this issue shall be analysed in later simulations and calculations.

There are numerous models which have been developed and used for representing the carbon cycle. The box models have been in use since 1957, when the four-box model was presented for the first time [10], Fig. 2.

Thereafter many variations have been introduced for a common use or for special purposes. A commonly used model is a three-box model, in which both the atmosphere and the surface ocean have been assumed to be well-mixed reservoirs, the deep ocean being a stagnant reservoir and the biosphere is omitted [11]. The ocean part of the box-models have been developed to include another surface box [12], or to describe the thermocline more accurately [13]. Because two-box ocean model was not accurate enough, a box-diffusion model was developed [14]. In this model the transfer from the well-mixed surface ocean into the deep ocean has been simulated by vertical eddy diffusion.

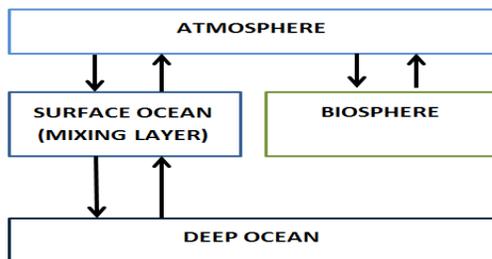


Fig. 2. A common four-box model of the global carbon cycle [10]

Complex simulation models have been introduced, which are based on the massive measurement data. Two different calculation

bases exist: Partial pressure of CO_2 in the surface sea [15] and the ocean inverse flux calculations [16]. The global estimates of ocean uptake have been calculated during the period from 1995 to 2000 for these two models. The results cannot be tested against the real flux values, because there is no commonly accepted theory in which way the carbon dioxide fluxes are distributed between the atmosphere, biosphere and the ocean.

The atmospheric CO_2 dissolves in the surface ocean according to Henry's law

$$[\text{CO}_2] = K_o(T, S, A) * f\text{CO}_2, \quad (4)$$

where $[\text{CO}_2]$ is concentration of CO_2 in the surface ocean, $f\text{CO}_2$ is fugacity (\sim partial pressure of CO_2 in the surface water with an error about 0.4%), and K_o is equilibrium constant as function of temperature (T), salinity (S), and alkalinity (A). The variations of salinity and alkalinity concentrations have minor influences and these effects can be omitted. When the surface ocean is in balance with the atmosphere, the atmospheric partial pressure of CO_2 can be used as a measure of the CO_2 fugacity. Therefore the dissolution depends mainly on the atmospheric CO_2 concentration and the surface ocean temperature. The dependence of CO_2 dissolution on the temperature is the basic reason for the carbon cycle between the atmosphere and the ocean. The colder waters of high latitude ocean dissolve CO_2 and the warmer waters of mid and low latitude ocean absorb CO_2 . The sea currents transport the cold waters to the low latitude zone, where the cold waters warm up and absorb CO_2 .

Dissolved CO_2 reacts with H_2O forming the compound H_2CO_3 , which dissociates to carbonate ions (CO_3^{2-}) and bicarbonate ions (HCO_3^-). The average oceanic pH of 8.15 -8.2 determines that the amounts of these three forms are: Carbonate ions 90%, bicarbonate ions 9%, and CO_2 1%. These reactions explain why the carbon amount in the ocean is about 70 - 100 times higher than calculated by the Henry's law in the distilled water.

Oceanic carbon is divided into four forms, which are dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate organic carbon (POC) and marine biota. POC is a fine particle portion of DOC, which is defined by separating with a $0.45 \mu\text{m}$ filter. POC has an important role in the biological pump, which converts CO_2 first

into organic carbon and then into CaCO_3 . As a final result is an oceanic sedimentation rate at which CaCO_3 precipitates on the ocean bed. This process is controlled mainly by biological processes and by the amount of POC. The sedimentation rate estimates vary in the broad limits from 0.09- 0.3 GtC/y [17] to an estimate that the whole amount of DOC (~1000 GtC) could sink to the ocean bed in less than one year [18].

The amount of DOC has been estimated to be 1000 GtC [19] and the amount of POC to be 30 GtC [20]. Because the average DIC concentration is 2.2 mol/t in seawater at 4°C, and the volume of the ocean is 1.384×10^{18} t, the total amount of DIC is estimated to be 36500 - 40000 GtC. The ocean surface layer (= mixing layer) is assumed to be 75 meters deep and the concentration of DIC at 15°C is 2.12 mol/t, which means that the surface ocean carbon (CSO) is 727 GtC calculated according to the present CO_2 atmospheric concentration of 400 ppm.

Before the industrialization the atmospheric CO_2 concentration was 280 ppm, which gives the total CO_2 amount of 595 GtC in the atmosphere (CIA). The relationship between CIA:DIC in 1750 was 1:63. In 2013 the amount of CIA was 845 GtC corresponding to the CO_2 concentration of 397 ppm and therefore the relationship CIA:DIC was 1:46. It is generally accepted that today there is an unbalance between CIA and DIC, because mankind has increased the amount of CIA very rapidly since 1750 and there has not been enough time to settle down into a new balance. There are two schools of thoughts about what is the capacity of the ocean to dissolve the atmospheric CO_2 into DIC and at which rate this dissolution can happen.

One approach could be called as "buffer factor" based estimation. The buffer factor means buffering of CO_2 exchange from air to seawater and it is also known as "Revelle factor" [7]. The Revelle factor value is about 14 in the high latitude waters and about 10 in equatorial waters. The buffer factor 10 means that a 10% increase of partial pressure of CO_2 can increase only 1% the total carbon amount in the ocean [7]. This approach leads to the net dissolving rate of about 2-3 GtC per year [13], which is not essentially depending on the atmospheric CO_2 concentration because of the buffering phenomenon.

The Revelle buffer factor approach creates a problem called "missing sink" of carbon [19]. If

the net dissolving rate of the ocean is only 2-3 GtC/y, the net CO_2 flux rate into atmosphere would be 7-8 GtC/y. Because the latter flux is about 5-6 GtC/y, there is a gap of 2-3 GtC/y in the present climate. The biosphere has been offered as a potential sink, but all researchers have not accepted it, because at the same time deforestation releases CO_2 [2]. There are studies which do not accept the almost constant buffer capacity of the ocean. The increased atmospheric CO_2 concentration can increase the buffer capacity by 2.5 to 6 times [21]. Other minerals like borate, kaolinite and clay minerals can essentially increase the storage capacity of CO_2 [22-23]. Some researchers have concluded that these buffers together means infinite buffer capacity [23].

Some clarity for the ocean's capacity to absorb CO_2 can be found in the 5 years long research study, where the data of 9618 hydrographic stations were collected on 95 cruises over all the oceans [24]. The result was that the oceans have absorbed, from 1800 to 1994, in total 118 GtC±19 GtC anthropogenic CO_2 . When the models and measurements are in conflict, in the natural sciences it is always a justified solution to use the direct measurements.

During the timespan from 1750 to 2013, the fossil fuel usage has released 395 GtC, and CO_2 atmospheric increase of CIA has been 240 GtC [25]. The difference of these two fluxes is 155 GtC. IPCC [2] estimates that the ocean has uptaken this 155 GtC and the rest 240 GtC of anthropogenic CO_2 has remained in the atmosphere. Two other scientific organizations NASA [3] and The Royal Society [26] estimate that currently about 50% of carbon released into the atmosphere by fossil fuel burning is absorbed by the ocean.

The conclusion is that there are great uncertainties in the carbon cycle figures and in the dissolution capacity of the ocean. It is scientifically justified to use the approach that the ocean has still the capacity to uptake the CO_2 . Because the well mixed surface ocean is in balance with the atmospheric CO_2 concentration, the ocean's temperature fluctuations can create short term fluctuations also into the atmospheric CO_2 concentration. Here we have also two schools of thoughts. One approach says that it is possible and another approach does not accept this kind of mechanism. Ice cores studies show that the atmospheric CO_2 changes lag behind

atmospheric temperature changes from a century to millennium [27,28]. A study of the present time shows that the same happens on the yearly scale, and the CO₂ concentration fluctuations are 11-12 months behind sea surface temperature [29].

2. DEVELOPMENT OF THE SEMI-EMPIRICAL 1DAOBM

The starting point for the development of the semi-empirical 1DAOBM is depicted in Fig. 3. It is easy to see that the yearly CO₂ increase in the atmosphere follows the sea temperature changes. The correlation is 0.83, and the r₂ is 0.69. The strongest El Nino years have the positive impacts on the CO₂ increase. Based on these findings I have developed a semi-empirical atmosphere-ocean-biosphere carbon model (1DAOBM), which is a four-box model. The

schematic picture of this model is depicted in Fig. 4.

The 1DAOBM is based on the following assumptions: 1) the anthropogenic and natural CO₂ are fully mixed in the atmosphere, having a residence time of about 3.9 years, 2) the dissolution pump flushes CO₂ from the atmosphere and the ocean dissolves CO₂, keeping the atmospheric δ¹³C in the dissolved flux, 3) the biosphere carbon cycle flushes CO₂ from the atmosphere and the plants assimilate CO₂, keeping the δ¹³C in -26, 4) the dissolution pump recycles CO₂ from the fully mixed surface ocean into the atmosphere, keeping in this flux the δ¹³C of the surface ocean, 5) the biosphere carbon cycle recycles CO₂ from the plants and the soil keeping the δ¹³C in -26, 6) the flux rate for the surface ocean into the deep ocean is based on the empirical relationship.

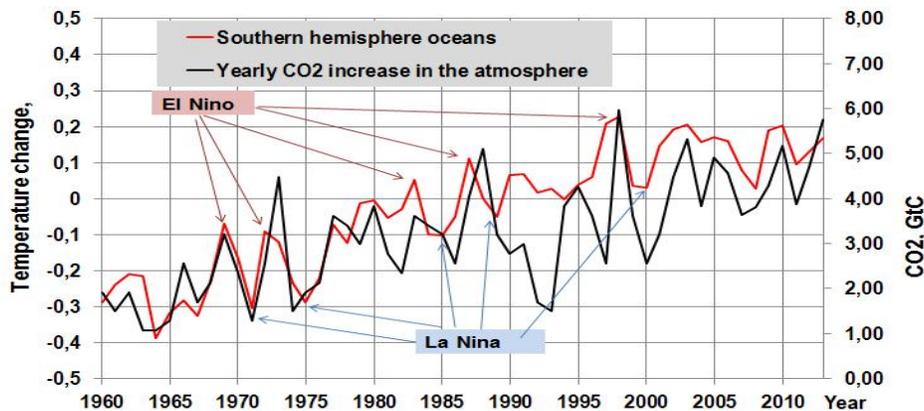


Fig. 3. Yearly CO₂ increase in the atmosphere and the temperature variations of the southern ocean i.e. the average of the sea temperatures of oceans 20N-20S and 30S-60S

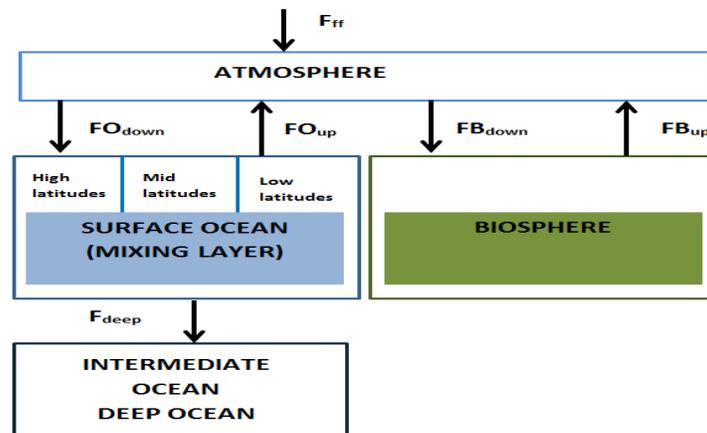


Fig. 4. Four-box model applied for the atmosphere-ocean carbon cycle in development of 1DAOBM. The fluxes are defined more closely in Table 2

The theoretical bases of these choices are explained in the introduction section. The most important choice is that there is no missing sink of carbon, but the ocean and the biosphere are capable of uptaking the CO₂ not found in the atmosphere. The ocean can continue to do absorbing in the future. The theoretical calculations of flux rate from the surface ocean into the deep ocean are not accurate enough, and therefore in 1DAOBM this part is represented by the empirical linear first order equation.

In reference [30] is a graphical presentation of the CO₂ concentration in sea water (ppmv) as a function of DIC and temperature (35‰ salinity and 2.35 meq/kg alkalinity). Originally, this graph was made by K. Holmen, but it is not available. I have digitized the graphs of CO₂ concentrations for 300, 350, 400, 500 and 600 ppm. Thereafter I have made 2nd order polynomial fitting for the CO₂ concentration graphs of 350 ppm and 500 ppm.

The DIC values can be calculated as functions of CO₂ and sea water temperature according to equations (5) and (6):

In the CO₂ concentration range of 280 ppm – 430 ppm:

$$DIC = 2.2 - 5.5774 \cdot 10^{-3} \cdot T - 8.631 \cdot 10^{-5} \cdot T^2 + 6 \cdot 10^{-4} \cdot (C-350) \quad (5)$$

In the CO₂ concentration range of 430 ppm – 600 ppm:

$$DIC = 2.255 - 5.114 \cdot 10^{-3} \cdot T - 6.84 \cdot 10^{-5} \cdot T^2 + 3 \cdot 10^{-4} \cdot (C-500) \quad (6)$$

In these equations DIC is dissolved inorganic carbon (mol/t), T is temperature (°C), and C is CO₂ concentration (ppm). These graphs are depicted in Fig. 5.

The DIC amount in CSO can be now calculated assuming that the mixing layer is 75 m deep, which I have divided into three parts: high latitude ocean 15%, mid latitude ocean 45%, and low latitude ocean 40%.

I have carried out two different simulations. The first simulations by 1DAOBM were carried out for finding out the anthropogenic CO₂ fractions in the atmosphere, in the ocean, and in the biosphere and the fluxes between these reservoirs. These simulations extend from 1750 to 2013. The second simulations have been carried out to find the short term fluctuations in the atmospheric CO₂ amounts, and they extend from 1960 to 2300.

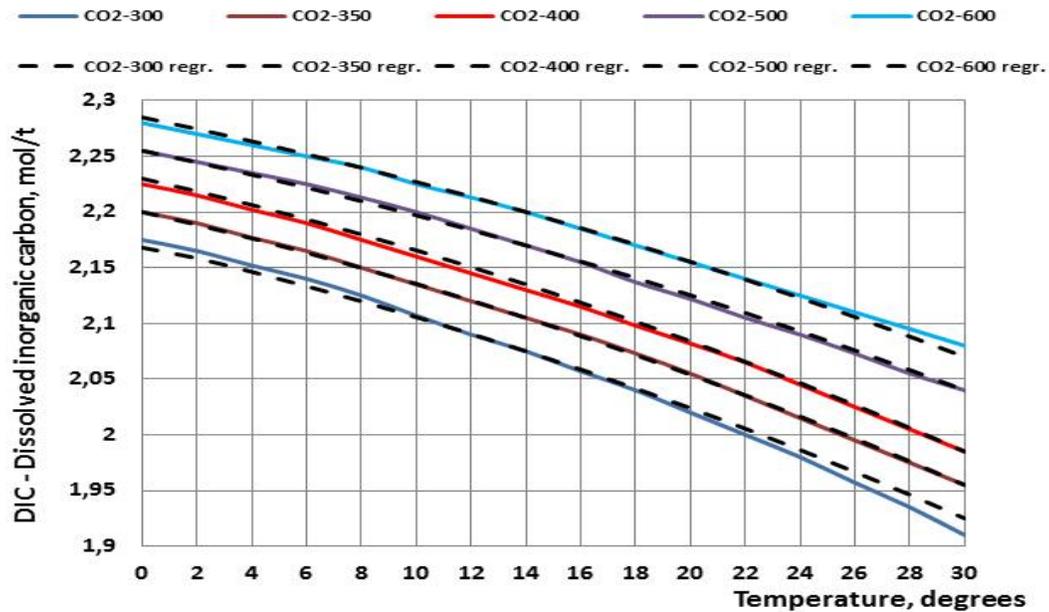


Fig. 5. DIC as a function of temperature and CO₂ concentration in sea water without buffer effect

3. ANTHROPOGENIC CO₂ FLUXES AND AMOUNTS

Because there are huge differences in the estimates of how much anthropogenic CO₂ actually is in the atmosphere, it is useful to analyze the anthropogenic CO₂ change in the atmosphere firstly with the simple terms. Total fossil fuel emissions from 1750 to 2013 have been 395 GtC [25] and CO₂ increase of at the same time in the atmosphere has been 234 GtC. If we assume that 234 GtC increase of CO₂ in the atmosphere to be all of anthropogenic origin, it would be 28% of the total 850 GtC as reported by IPCC [2]. This is not true for three reasons: 1) the atmosphere is an almost-ideal mixing chamber by diluting an annual fossil fuel increase efficiently into the large mass of the total atmospheric CO₂, 2) the carbon cycle removes anthropogenic CO₂ from the atmosphere into the ocean and into the biosphere, and then replaces the same amount mainly with natural CO₂

available in these reservoirs, and 3) the direct $\delta^{13}\text{C}$ measurements in the atmosphere show that the assumed anthropogenic CO₂ level of 28% do not match with $\delta^{13}\text{C}$ measurements. The calculation basis for different variables is listed in Table 2.

The dissolution pump between the atmosphere and the ocean cycles both natural and anthropogenic CO₂ in and out from the atmosphere, keeping the ¹³C fraction constant. The uptake of the ocean is basically a physical process, and it is not selective in dissolving different isotopes of CO₂. As explained in section1, the plants are selective in using CO₂ isotopes, preferring the isotope ¹²C in some degree. The $\delta^{13}\text{C}$ of plants is lower (-26‰) than in the atmosphere (-8.4‰ presently). Therefore, the carbon cycle between the atmosphere and the biosphere removes a little bit lower amount of anthropogenic CO₂. The amount is only slightly smaller, because the ¹²C/C_{tot} is 0.9892.

Table 2. The calculation basis for variables in the 1DAOBM simulation. The amounts are in GtC and fluxes are in GtC/y. The fluxes are introduced in Fig. 4.

Variable acr.	Variable name	Calculation formula
FO _{tot,down}	Total dissolution carbon pump flux from the atmosphere into the ocean	$100 + \Delta\text{CIA}_{\text{tot}}$
FLUSH _{AO} -%	Flush-% of the dissolution pump from the atmosphere into the ocean	$100 * \text{FO}_{\text{tot,down}} / \text{CIA}_{\text{tot,n}}$
FO _{ant,down}	Anthropogenic dissolution carbon pump flux from the atmosphere into the ocean	$\text{FLUSH}_{\text{AO}}\% * \text{CIA}_{\text{ant,n-1}} / 100$
FO _{tot,up}	Total dissolution carbon pump flux from the ocean into the atmosphere	100
FLUSH _{OA} -%	Flush-% of the dissolution pump from the ocean into the atmosphere	$100 * \text{FO}_{\text{tot,up}} / \text{CSO}_{\text{tot,n}}$
FO _{ant,up}	Anthropogenic dissolution carbon pump flux from the ocean into the atmosphere	$\text{FLUSH}_{\text{OA}}\% * \text{CSO}_{\text{ant,n-1}} / 100$
FB _{B,down}	Total biosphere carbon cycle flux from the atmosphere into the biosphere	$0.9891734 * (120 + \Delta\text{CIA}_{\text{tot}})$
FLUSH _{AB} -%	Flush-% of the biosphere carbon cycle from the atmosphere into the biosphere	$100 * \text{FB}_{\text{tot,down}} / \text{CIA}_{\text{tot,n}}$
FB _{ant,down}	Anthropogenic biosphere carbon cycle flux from the atmosphere into the biosphere	$\text{FLUSH}_{\text{AB}}\% * \text{CIA}_{\text{ant,n-1}} / 100$
FB _{ant,up}	Anthropogenic biosphere carbon cycle flux from the biosphere into the atmosphere	$0.47 * \text{FB}_{\text{ant,down}} + 0.1 * \text{FB}_{\text{ant,down,n-8}} + 0.3 * \text{FB}_{\text{ant,down,n-50}} + 0.06 * \text{FB}_{\text{ant,dow,n-70}}$
F _{deep}	Anthropogenic CO ₂ flux from the surface ocean into the intermediate & deep ocean	$K_1 * (\text{CSO}_n - \text{CSO}_{1750})$; $K_1 = 0.18$
ΔCSO	Anthrop. CO ₂ change in the surface ocean	$\text{FO}_{\text{ant,down}} - \text{FO}_{\text{ant,up}} - F_{\text{deep}}$
ΔCDO	Anthrop. CO ₂ change in the deep ocean	$F_{\text{deep,n}} - F_{\text{deep,n-1}}$
ΔCIB	Anthrop. CO ₂ change in the biosphere	$\text{FB}_{\text{ant,down}} - \text{FB}_{\text{ant,up}}$
ΔCIA	Anthropog. CO ₂ change in the atmosphere	$F_{\text{ff}} + \text{FO}_{\text{ant,up}} + \text{FB}_{\text{ant,up}} - \text{FO}_{\text{ant,down}} - \text{FB}_{\text{ant,down}}$
CSO _{tot}	Total CO ₂ in the surface ocean	Equations (5) and (6)

Therefore, the biosphere can also remove anthropogenic CO₂ and recycle it back into the atmosphere.

The formulas in Table 2 are simple and self-explaining, except two of them. The flux $FB_{ant,up}$ is based on the results of the reference [31]. According to this study, about 50% of the CO₂ assimilated by the biosphere is respired back by the plants in a year (47% selected), and 10% will recycle back from the detritus after a turnover time of less than 10 years (8 years selected). The rest of CO₂ is converted into soil organic carbon, and its turnover time varies a lot depending on the source. In this study, I have used a turnover time of 50 years for 30% of CO₂ flux and 70 years for 6% of CO₂ flux. About 5...6% of soil organic carbon will not recycle back into the atmosphere.

I have selected the flux rates of the carbon pump to be in the dissolution pump 100 GtC/y and in the biosphere carbon cycle to be 120 GtC/y [19]. The overall removal-% in the present atmosphere is therefore about $100 * 220 \text{ Gt} / 845 \text{ Gt} = 26\%$. The global sea surface temperatures for the different zones are from the reference [32], global annual fossil fuel budget values from the reference [25], and the global CO₂ concentration values from the reference [33]. In this simulation, I have used the average ocean temperature in calculating the CO₂ amount in the surface ocean.

The only empirical parameter in these simulations is parameter K_1 , which is used in

calculating the flux F_{deep} . The value of 0.18 is selected so that the $CSO_{ant} = 23.4 \text{ GtC}$ of the simulation is the same as calculated using the equations (4) and (5) from 1750 to 2013. This selection states that the sum of $CDO_{ant} + CSO_{ant}$, integrated from 1750 to 1994, is together 115.8 GtC. It is very close to the observed value of $118 \pm 19 \text{ GtC}$ [24]. According to the study [24], the majority of the anthropogenic CO₂ in the ocean is confined to the thermocline (< 1000 m depth) and nearly 50% at the depths above 400 m.

The mixing layer of the ocean keeps the CO₂ in balance with the atmospheric CO₂. There is a driving force from the surface ocean into the deep ocean, because the surface ocean is supersaturated with respect to calcium carbonate but the deep ocean is undersaturated [19]. The regional conditions of the surface ocean may vary but in the global scale the CSO amount controls the F_{deep} flux into the deep ocean.

The simulations have been carried out using spread sheet calculations with one year steps. If the values of former years have been applied in a formula, it can be noticed from the subscript_n. The calculations do not include any iterative operations. The results are depicted in Fig. 6.

Fig. 6 demonstrates well that the carbon cycle fluxes move bigger amounts of anthropogenic CO₂ than what is available yearly as a fresh flux in the form of fossil fuel emissions. This process is further illustrated in Fig. 7 in which the numerical values are based on the simulation calculations.

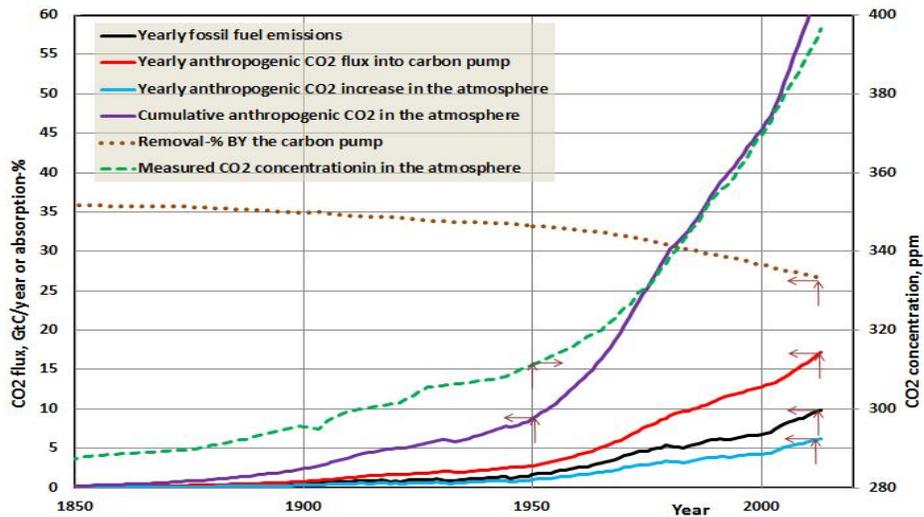


Fig. 6. The calculated anthropogenic CO₂ fluxes and amounts according to 1DAOBM

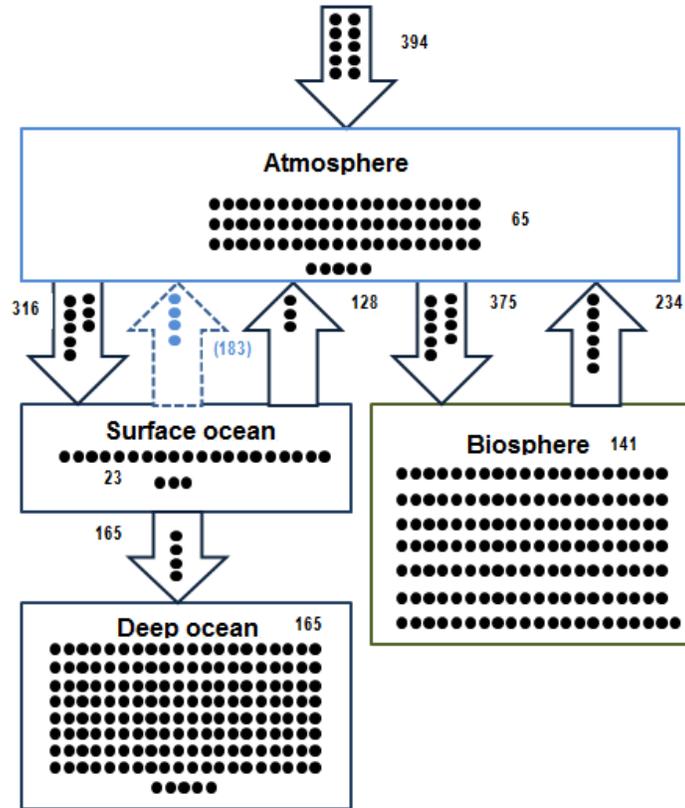


Fig. 7. The illustration of the carbon cycle effects in diluting and removing the anthropogenic CO₂ from the atmosphere

The numerical values correspond to the cumulative values of anthropogenic fluxes integrated from 1750 to 2013 and the reservoirs in 2013 (black font). The exception is the value 183 (blue font in brackets) corresponding to the natural CO₂ flux from the ocean into the atmosphere. One dot represents 1 GtC of CO₂. The black dots inside the arrows represent yearly anthropogenic flux rates in 2013. The blue dots represent the natural yearly CO₂ flux rate in 2013 recycling back from the ocean into the atmosphere and replacing anthropogenic CO₂.

4. SHORT TERM FLUCTUATIONS OF THE ATMOSPHERIC CO₂ BY 1DAOBM

As illustrated in Fig. 3, the CO₂ amounts in the atmosphere seem to follow the temperature changes of the ocean. The first simulations already show what the basic reason for this relationship is: The strong CO₂ flux of the dissolution pump between the atmosphere and the ocean. I carried out simulations using basically the same arrangement as in the first simulations, with two exceptions. The time period was from 1950 to 2013, and the actual ocean temperatures of high, mid, and low latitudes were applied in calculating the dissolution capacity of the ocean. Because of these choices, the value of parameter K₁ was 0.1886. The net fluxes of carbon cycles are depicted in Fig. 8.

The simulation in Fig. 8 shows that the dissolution carbon pump flux fluctuates much more than the biosphere carbon cycle flux. In Fig. 9 are depicted the measured and calculated CO₂ fluxes into the atmosphere. Because the anthropogenic CO₂ amount in the atmosphere in 2013 is 65.0 GtC and the measured total CO₂ increase from 1750 to 2013 is 248.3 GtC, the gap of these amounts of 183.3 GtC has a natural origin. This CO₂ comes from the ocean and the natural CO₂ flux from the ocean is depicted also in Fig. 9. This flux varies mainly according to the temperature changes of the ocean. The accumulated natural CO₂ from the ocean into the atmosphere is only 0.7% of the total CO₂ recycling flux during the years 1950-2013.

In the simulation calculations it was easy to find out that the atmospheric CO₂ changes are

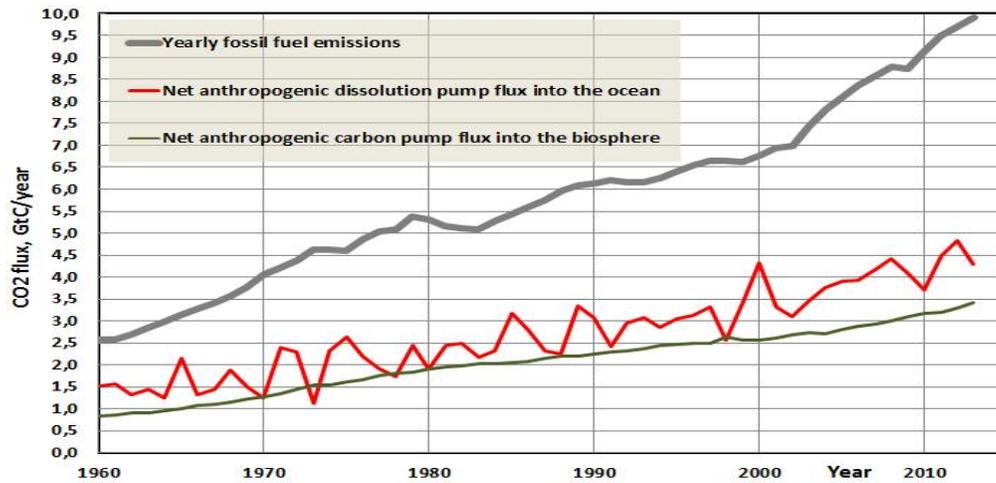


Fig. 8. The net fluxes of the dissolution pump and the biosphere carbon cycles from 1960 to 2013

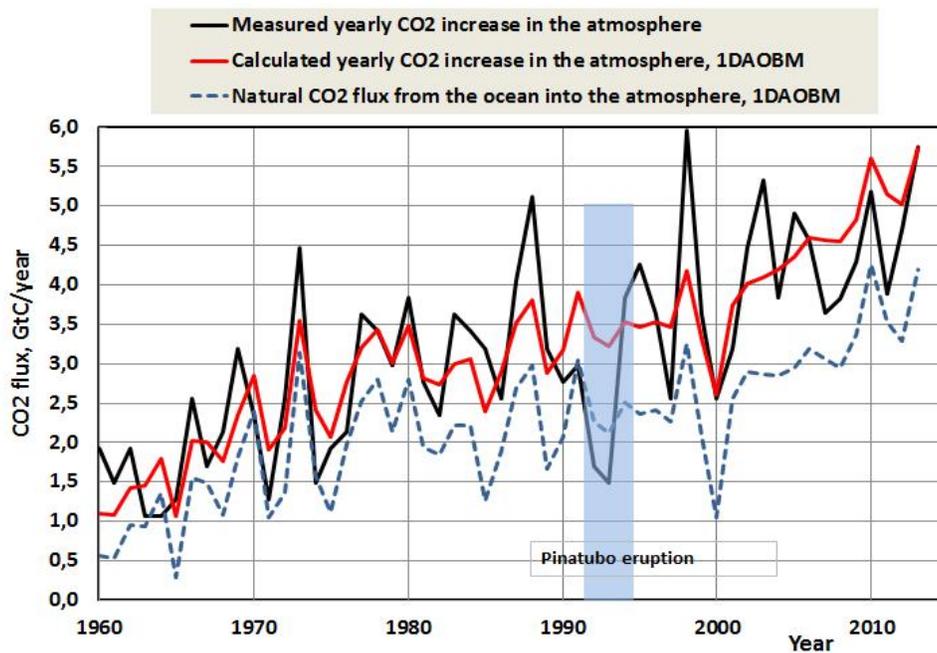


Fig. 9. The measured and calculated CO₂ fluxes into the atmosphere

lagging in about a one year time lag behind the ocean temperature changes. This time lag has been applied in the 1DAOBM calculations. This finding confirms the same result found in the reference [29].

There is an anomaly in the 1DAOBM during the years 1991-1993. This is the time, when Pinatubo eruption ejected about 20 Mt sulphur dioxide and dust into the upper part of the

troposphere. The shortwave radiation at the Earth's surface reduced about 4 Wm² [34]. Strangely enough this huge deviation during 1.5 years' time had hardly any effects on the surface temperature as one can see in Fig. 3. Also CO₂ fluxes and inventory changes have acted in an unpredicted way. The CO₂ amount inventory change in the atmosphere deviated into negative direction, being thus "in the wrong direction". It is difficult to find a good reason why in those

conditions the ocean would have absorbed a high amount of CO₂ or the biosphere would have suddenly used much more CO₂, when the shortwave radiation amount had strongly decreased. So far there is no good explanation for this anomaly.

The regression analysis shows that the correlation between the measured CO₂ flux into the atmosphere and 1DAOBM is 0.87, $r_2 = 0.75$, and the standard error of the estimate is 0.68 GtC/y. The model explains fairly well the real measured variations of the total CO₂ in the atmosphere.

5. FUTURE PROJECTIONS AS SIMULATED BY 1DAOBM

The 1DAOBM can be used to simulate the future projections of CO₂ fluxes and concentrations in the atmosphere. I have carried out a simulation using fossil fuel emission values, which are close to the projection RCP4.5 also used by ICPP [35]. In this projection is a linear growth rate of fossil fuel emissions from the present level of 36.7 Gt CO₂ (=10 GtC) to 42 Gt CO₂ (=11.5 GtC) up to 2040, and thereafter the emissions decline before 2080 before levelling off to 15 Gt CO₂ (=4.1 GtC). In my simulation, the fossil fuel emission rate has a parabolic form with the same

maximum value at 2040 and the same minimum value at 2100 as RCP4.5. The simulation results are depicted in Fig. 10. The temperature has been assumed to stay at the present level.

There are differences in the CO₂ concentration trends between IPCC [2] simulations and 1DAOBM. In 2040 the concentrations are still relatively close to each other: 466 ppm (IPCC) versus 468 ppm. In 2100 IPCC's value is 538 ppm and staying at this level until 2300, but 1DAOBM's value is 468 ppm in 2100 and thereafter decreasing steadily to the value of 412 ppm in 2200. According to 1DAOBM the ocean continues to uptake CO₂, which leads to the decreased CO₂ concentration after the maximum value of 498 ppm in year 2059. IPCC's model applies the Global Change Assessment Model (GCAM). It looks like this model keeps the high CO₂ concentration level in the atmosphere probably based on the long lifetime estimate of anthropogenic CO₂. IPCC phrases this mechanism [2] that "Within several decades of CO₂ emission, about a third to half of an initial pulse of anthropogenic CO₂ goes into the land and ocean, while the rest stays in the atmosphere". There is no description of mixing capacity of the atmosphere or any physical description in which way a part of an initial pulse actually departs from the atmosphere. In reality,

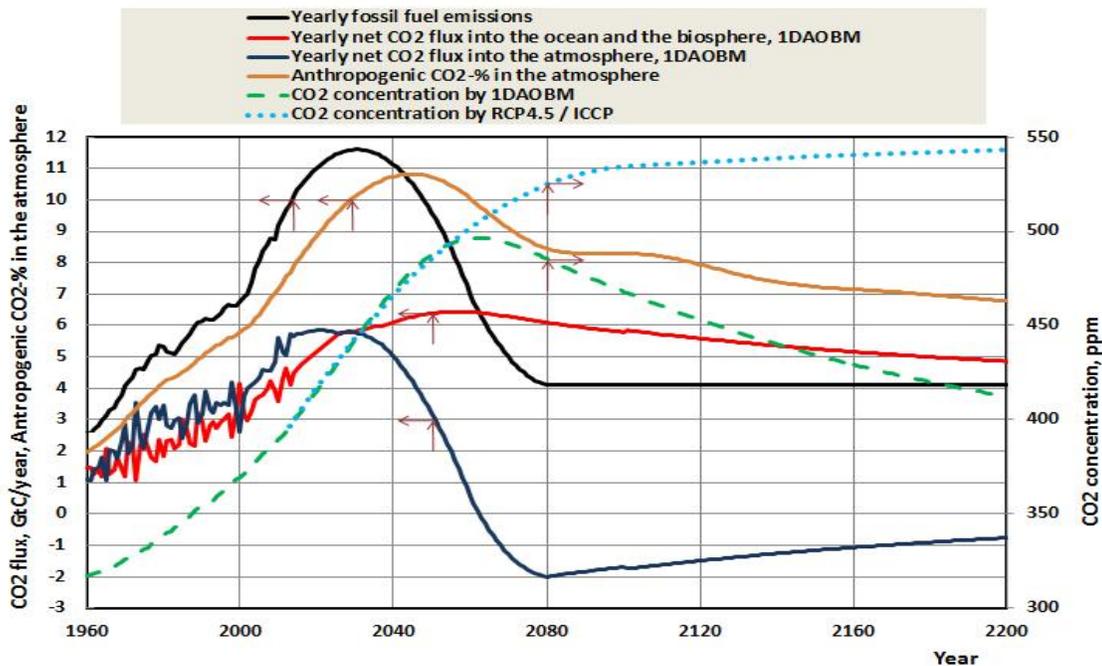


Fig. 10. The simulation results of the fossil fuel emissions close to projection RCP4.5

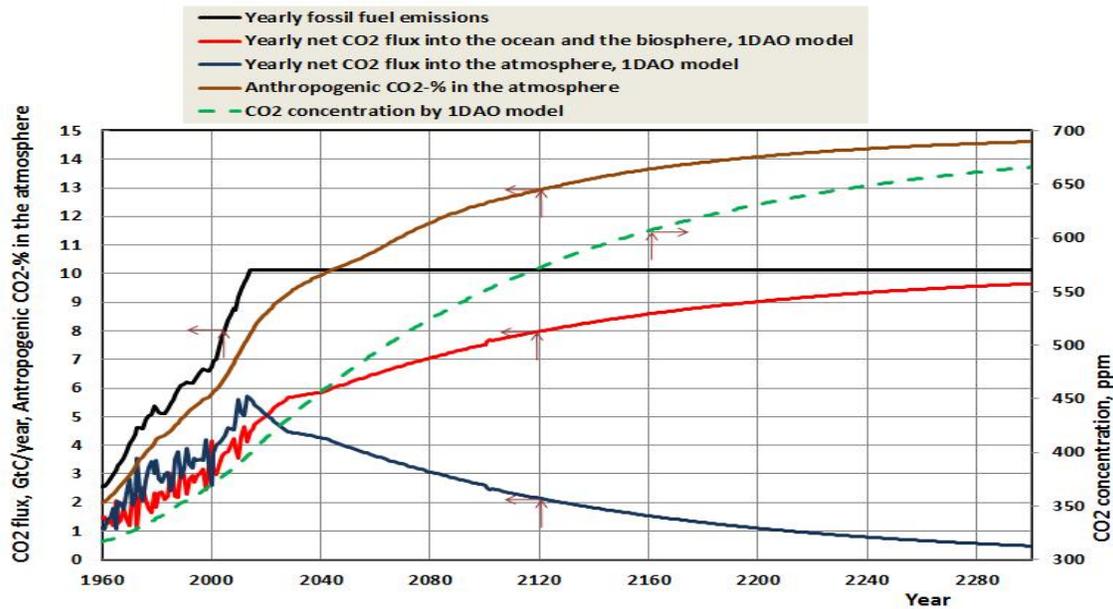


Fig. 11. The future projection of CO₂ fluxes for the fossil fuel emission rate of 10 GtC/y from 2015 forward

GCAM seems to retain the major part of anthropogenic CO₂ in the atmosphere, when the initial emission pulse starts to decrease.

In above Fig. 11 possible future trends for the fossil fuel projection are depicted, which keeps the present level 10 GtC/y from 2015 to 2300.

The simulation in Fig. 11 shows that the balance value of CO₂ has not been reached even up to 2300, because the flux rates have not yet levelled out. The estimate of the CO₂ balance concentration after 2300 is 670-690 ppm.

6. RESULTS AND DISCUSSION

Check calculations can be carried out in order to find out if the 1DAOBM simulations could explain the low anthropogenic $\delta^{13}\text{C}$ in the atmosphere. The value of natural CO₂ varies depending on the sources. According to reference [5], $\delta^{13}\text{C}$ value of -7‰ is in equilibrium with CO₂ dissolved in the hydrosphere and in marine calcium carbonate [5]. According to reference [36], the $\delta^{13}\text{C}$ before the industrialization has been at the level -6.5‰ in the atmosphere. Thereafter the value has started to increase being at the level -6.75‰ in about 1900. I have used this value as a reference without anthropogenic influence.

The researchers have noticed that in the ocean, there has not been found a generally accepted

$\delta^{13}\text{C}$ value without the anthropogenic influence. Even the present level is not clear. I have used as a reference value without anthropogenic influence -9.0‰. The present atmospheric $\delta^{13}\text{C}$ values are from reference [37]. The calculated $\delta^{13}\text{C}$ values in the atmosphere and in the ocean are depicted in Table 3. The values have been calculated according to equation (3).

There is almost a perfect match between the calculated and measured $\delta^{13}\text{C}$ values in the atmosphere. The same cannot be concluded from the IPCC's approach with the anthropogenic CO₂ fraction of 28% in 2013, because it would lead into the -12.9‰ of $\delta^{13}\text{C}$.

In reference [38], from -0.7‰ to -0.9‰ (± 0.3 ‰) of $\delta^{13}\text{C}$ decrease has been measured in the surface water sponges of Caribbean and South Pacific Ocean from 1900 to 1990. The calculated decrease by 1DAOBM has been -0.6‰, which is close to the measured values. The decreased $\delta^{13}\text{C}$ values both in the atmosphere and in the ocean are mainly due to the anthropogenic emissions of fossil fuels. The 1DAOBM can explain very well both changes and extremely well that of the atmosphere.

The simulation calculations show that the anthropogenic fraction of CO₂ in the atmosphere in 2013 is only 7.7%. This result is based on the diluting effect of the carbon cycle between the

Table 3. The anthropogenic fraction of CO₂ and δ¹³C in the atmosphere and in the ocean according to the 1DAOBM simulations and reference [37].

Year	The atmosphere		The ocean	
	Anthropogenic fraction of CO ₂ , 1DAOBM, %	δ ¹³ C by 1DAOBM, ‰	δ ¹³ C reference, ‰	δ ¹³ C by 1DAOBM, ‰
1900	0.4	-6.8	-6.75	-9.0
1950	1.3	-7.0	-6.9	-9.1
1977	4.0	-7.6	-7.5	-9.3
1988	4.8	-7.8	-7.8	-9.4
2000	5.8	-8.0	-8.0	-9.5
2006	6.5	-8.1	-8.2	-9.5
2013	7.7	-8.4	-8.4	-9.6

atmosphere, the ocean, and the biosphere. This result differs totally from IPCC's value of 28% [2], but it is close to real observations [7] and [36]. This low fraction 7.7% of anthropogenic CO₂ explains extremely well the observed δ¹³C of -8.4‰ in the present atmosphere, and it explains why the δ¹³C remains so high in the atmosphere.

The simulation of RCP4.5 projection shows the big differences between the GCAM model simulation and 1DAOBM. In the increasing phase of CO₂ emissions up to 2050, the atmospheric CO₂ concentrations follow each other fairly well. When the emission rate starts sharply to decline, the CO₂ concentrations depart. In GCAM simulation the CO₂ continues to increase to the year 2090 and stays at this level for more than a century but according to 1DAOBM there is an almost symmetrical decline in the same way as the increasing phase of emissions. There are probably two fundamental reasons. Firstly, in the GCAM simulation, the residence time is assumed to be more than 100 years, and secondly, the ocean does not dissolve the atmospheric CO₂, in the GCAM simulation, according to the same process as the increasing phase.

As far as more complicated methods cannot show a trustworthy method for calculating the missing sink reservoir, simple models like 1DAOBM developed in this study can be used to simulate atmosphere–ocean fluxes, which corresponds the observations with very good accuracy.

7. CONCLUSION

The results of the 1DAOBM show that it has a good capability to follow the temperature and CO₂ concentration changes. The standard error is small enough in flux rate estimates for simulations of the history and the future trends. For example, the CO₂ increases in the atmosphere at the present time are about 5 GtC

annually. The 1DAOBM's standard error is 0.68 GtC, which is 13.6% from the present flux rate. This can be compared to the results of complicated models like that in reference [16] in which the oceanic uptake flux of the anthropogenic carbon in the period between 1995 and 2000 has been 2.2±0.3 or 1.9±0.7 GtC/y, depending on the estimation method. In this study according to a simple 1DAOBM, the same flux has been 3.25±0.7 GtC/y. The 1DAOBM leaves no room for a missing sink of carbon, but the complicated model leaves this question open. The direct measurements of anthropogenic carbon in the ocean and in the atmosphere support the results of 1DAOBM simulations.

From Fig. 9 a conclusion can be drawn that the ocean is outgassing (absolving) more CO₂ during the El Nino years and absorbing more CO₂ during the La Nina years than 1DAOBM actually calculates. The CO₂ flux rates into the ocean and into the atmosphere in Fig. 8 and 9 and very spiky and therefore there can be a timing problem in fitting together the measured and calculated flux rates. As realized before, I have used 12 months' time delay between the ocean temperature change and the outgassing of CO₂ into the atmosphere. I applied a slight smoothing to both measured and 1DAOBM flux values using the formula $0.5 \cdot F_{n-1} + F_n + 0.5 \cdot F_{n+1}$. This calculation method improves the correlation r_2 from 0.75 to 0.86.

The calculations of this study do not support the findings of earlier studies, which state that the residence time of both natural and anthropogenic CO₂ is about in the range 5.0-7.5 years. The simulations represented in Fig. 10 show that residence times are longer. From the differences between the peak value of the emission rate F_{ff} and the peak values of CO₂ concentration changes, two residence times can be identified.

The residence time of the anthropogenic CO₂ change in the atmosphere is 15 years, being the same as the longest values of some residence time studies [5], and the residence time of the total CO₂ concentration in the atmosphere is 32 years.

The simulations confirm the fact that the emission rate change to the CO₂ concentration changes does not take place in one ideal mixing chamber. The actual situation is described in Fig. 4 with a four box-model. The atmosphere and the surface ocean can be described with an ideal mixer, the biosphere with four parallel plug flow reactors with four different residence times, and the intermediate & deep ocean as an outlet of the system. Three of these boxes / reactors have recycling fluxes. The simulations are a practical way to determine the theoretical residence times.

Even though the residence times determined in this study are longer than in majority of other studies, the results of the atmospheric anthropogenic CO₂ fractions do not support the values used by IPCC, but are very close to the measured values.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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