



Timescales of Anthropogenic and Total Carbon Dioxide (CO₂) in the Atmosphere

Antero Ollila^{1*}

¹Department of Civil and Environmental Engineering (Emer.), School of Engineering, Aalto University, Espoo, Otakaari 1, Box 11000, 00076 AALTO, Finland.

Author's contribution

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

Article Information

DOI: 10.9734/PSIJ/2016/27004

Editor(s):

- (1) Mohd Rafatullah, Division of Environmental Technology, School of Industrial Technology, Universiti Sains Malaysia, Malaysia.
- (2) Christian Brosseau, Distinguished Professor, Department of Physics, Université de Bretagne Occidentale, France.

Reviewers:

- (1) Sylvester Odiana, University of Benin, Benin City, Nigeria.
 - (2) Bharat Raj Singh, Dr. APJ Abdul Kalam Technical University, Lucknow, India.
 - (3) António Félix Flores Rodrigues, University of the Azores, Portugal.
- Complete Peer review History: <http://www.sciencedomain.org/review-history/15789>

Original Research Article

Received 14th May 2016
Accepted 22nd June 2016
Published 14th August 2016

ABSTRACT

The author has enhanced the original one dimensional semi-empirical atmosphere-ocean-biosphere model 1DAOBM based on the four-box presentation. The improved 1DAOBM-2 contains two major parameters, which have been tuned to adjust the total CO₂ net flux rate and the anthropogenic net flux rate from the surface ocean into the deep ocean based on the observed values. The surface ocean part is based on the known dissolution chemical equations according to Henry's law depending on the atmospheric CO₂ concentration and the surface ocean temperature. Simulations have been used to calculate the dynamic responses to the step changes from the actual fossil fuel rate to zero in 1964. The results show that the anthropogenic CO₂ decay rate follows very accurately the observed decay rate of radiocarbon ¹⁴C having the residence time of 16 years. This is the expected result according to nature of anthropogenic CO₂ in the system of the atmosphere, the ocean and the biosphere. The decay rate of the total CO₂ in this system is much longer having the residence time of 55 years matching the adjustment time of 220 years. The simulations of the atmospheric net CO₂ rate by 1DAOBM-2 from 1960 to 2013 confirms the earlier results that the coefficient of determination $r^2 = 0.75$ ($r^2 = 0.81$ eliminating the Pinatubo eruption effects). The simulations also show that the present anthropogenic CO₂ fraction in the atmosphere is 8.0%, and it explains the observed $\delta^{13}\text{C}$ value of -8.4‰ extremely well. The problem of the sink

*Corresponding author: E-mail: aveollila@yahoo.com;

between the ocean and the biosphere could not be solved totally. A mass balance study shows that before 1956, the ocean and/or the biosphere acted as a source for the total CO₂ increase in the atmosphere and thereafter as a sink. This study suggests that the division ratio between the ocean and the biosphere is 60% / 40% for the period from 1750 to 2013. The high correlation between the ocean uptake and the net increase of the total atmospheric CO₂ strongly indicates that the ocean has been the sink after 1956.

Keywords: Residence times; timescales; atmosphere-ocean-biosphere model; CO₂ ocean sink; biosphere sink; atmospheric anthropogenic CO₂ and $\delta^{13}\text{C}$; ocean uptake; global warming.

1. INTRODUCTION

The major objective of this paper is to analyse, why the timescales are different for the anthropogenic CO₂ and for the total CO₂ changes in the atmosphere and why the decay timescales are different from the timescales of annual changes. These analyses include also the assessment, why the timescales of the published research studies show huge variations from 2 years to more than 1000 years.

Another objective is to show that the enhanced one dimensional semi-empirical atmosphere-ocean-biosphere model 1DAOBM-2 based on the original 1DAOBM developed by the author [1] is in line with the observed measurements and can therefore 1) simulate the decay rates of the

anthropogenic and the total CO₂ in the atmosphere, 2) calculate the portion of anthropogenic CO₂ in the atmosphere and in the ocean. The 1DAOBM-2 is based on the mass balance calculations and on Henry's law and it can also 3) represent the overall uptake CO₂ rate of the ocean and the biosphere, 4) explain that the annual fluctuations of the ocean uptake CO₂ flux rates depend on the atmospheric CO₂ concentration fluctuations and on the annual surface ocean temperature fluctuations, 5) explain that the annual fluctuations in the atmospheric total CO₂ amount depend mainly on the ocean uptake changes.

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

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}	CO ₂ flux into the deep ocean
F _{out}	Total CO ₂ flux from the atmosphere
F _A	CO ₂ flux into the atmosphere
FB	Biosphere carbon cycle flux
FO	Dissolution carbon pump flux
FN	Net CO ₂ flux from the atmosphere into the ocean
FLUSH-%	Flush-% of a carbon pump
IPCC	Intergovernmental Panel on Climate Change
T	Residence time
T _{adj}	Adjustment time
$\delta^{13}\text{C}$	A unit of measure of ¹³ C isotope

Subscript_{dn} means downwards, subscript_{up} means upwards, subscript_{ant} means anthropogenic CO₂, subscript_{nat} means natural CO₂, subscript_{tot} means total CO₂ (natural + anthropogenic), subscript_A means the atmosphere, subscript_O means the ocean, subscript_B means the biosphere, subscript_n means year n

There are several timescales which are commonly used as time delays describing the time required for each type of change in the atmospheric CO₂ concentration. A comprehensive study of the relationships between the timescales can be found in the paper of O'Neill et al. [2]. Usually these timescales are defined or approximated for the first order system. This means a system with one main time constant, as it is a case also in this paper.

The following timescales can be used interchangeably (marked with T): residence time, turnover time, (mean) lifetime, and e-folding time. Residence time is the same as the time constant of the first order system. It means that after the residence time the output of a step change has happened to 63.2% and 36.8% (=100/e) of the change is still left.

Another useful timescale is relaxation time or adjustment time (marked with T_{adj}), which means the time needed for a perturbed system to return to equilibrium or to steady state. Because theoretically T_{adj} would be infinitely long, in practice T_{adj} is approximated by multiplying the residence time by four: T_{adj} = 4 T. At this time moment a step change has reached the level of 98.3% from the final equilibrium value. Sometimes, a half lifetime is also used. A half-time means the time when 50% of the change has happened. For the first order system a half time = ln2/k = 0.693/k and T is 1/k, where k is the first order rate constant. Therefore in the first order system the half-time = 0.693 * T.

The four box model of carbon cycle is depicted in Fig. 1. The enhanced 1DAOBM-2 is based on this principle.

2. THE EVALUATION OF THE DYNAMICAL CO₂ CONCENTRATION CHANGES

One of the challenges of the timescale studies seems to be that the researchers do not always make a clear cut between the behaviour of two major CO₂ isotopes fluxes/amounts, which are the anthropogenic CO₂ and the total CO₂. The CO₂ in nature is the mixture of the carbon isotopes ¹²C and ¹³C, in which ¹³C has a portion of about 1%. The measurement unit of ¹³C proportion is δ¹³C. The δ¹³C of the natural CO₂ is about -7‰ corresponding to the portion of 1.11585% [3].

In this paper the term "total CO₂" has been used for the mixture of natural and anthropogenic CO₂

flux or amount. The Suess Effect shifts continuously the isotopic ratio of both ¹³C and ¹⁴C in any reservoir of the carbon cycle. The change of δ¹³C value is due to the combustion of fossil fuels. The typical δ¹³C values in the present time are [4,5]: the atmosphere -8.4‰, the surface ocean from +1.2‰ to +1.6‰, the biosphere -26‰, and the fossil fuels -28‰.

The isotope ¹⁴C is also called bomb ¹⁴C or radiocarbon, because it originates from the nuclear bomb tests in the atmosphere from 1945 to 1964 and it is radioactive by nature. The isotopes of ¹³C and ¹⁴C can be labelled [1], because their concentrations can be measured in the reservoirs of the CO₂ recycling system as illustrated in Fig. 1. This property gives an opportunity to track their transfer rates between the reservoirs and to check the calculations of any models, if they really match the observations. The total CO₂ amounts can be checked very accurately in the atmosphere with direct concentration measurements. The total and anthropogenic CO₂ amounts in the ocean are also based on the measurements but their amounts are not so accurate.

The decay curve of the ¹⁴C can be combined the some of the worldwide measurements carried out since 1950s [6-8] and this is illustrated in Fig. 2. The measured δ¹⁴C values differed in the northern and southern hemisphere in the beginning, because the nuclear tests were carried out in the northern hemisphere until 1964 but after 1968 there is no essential difference. The average value of northern and southern hemisphere measurements is depicted in Fig. 2.

The simulated decay rate with a residence time of 16 years gives a very good fit. The same value was found by Essenhigh [9] but the value of 7.5 years is clearly too short. This result shows the important feature of the CO₂ recycling system, that a relatively small increase of radiocarbon, is flushed away from the atmosphere into the ocean and into the biosphere. This is based on the fact that the removal processes – i.e. the fluxes FO_{dn} and FB_{dn} remove or flush a huge amount of CO₂ from the atmosphere into the other reservoirs (today about 25% of the total mass of the atmosphere each year), because they do not make practically any difference between the different CO₂ isotopes. It is true that the plants prefer the ¹²C isotopes but this effect is fairly small [1]. That is why these two fluxes FO_{dn} and FB_{dn} contain the same mixture of carbon isotopes as they are found in the atmosphere.

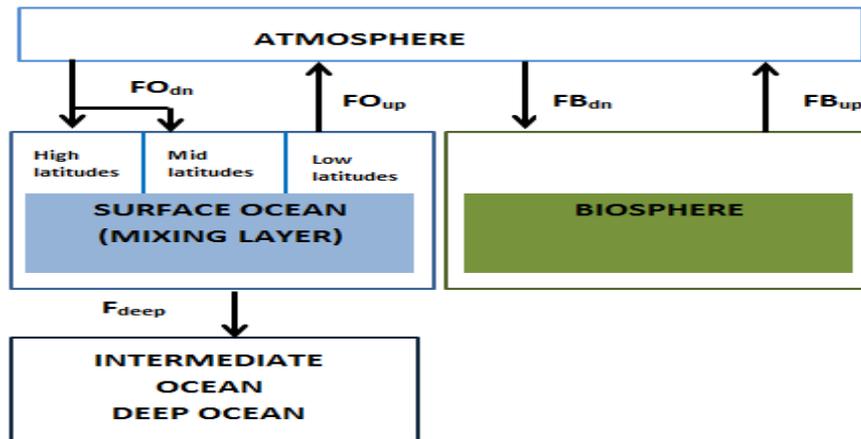


Fig. 1. The four box model of 1DAOBM-2

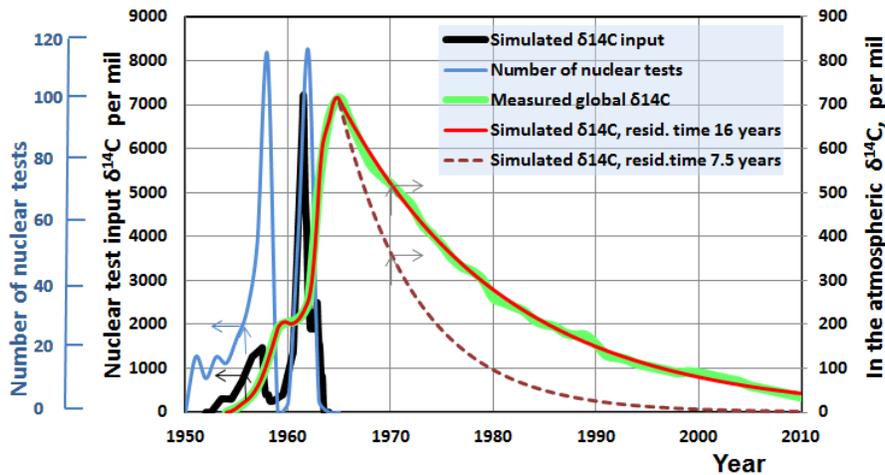


Fig. 2. The number of nuclear tests, the simulated $\delta^{14}\text{C}$ input values, the measured $\delta^{14}\text{C}$ values of radiocarbon and two simulated decay rates with 7.5 and 16 years residence times

The same mechanism applies to the fluxes recycling back into the atmosphere. The FO_{up} flux has the same mixture of carbon isotopes as there is in the surface ocean at the moment of the reflux flow. The radiocarbon concentration of the flux FB_{up} is more complicated as described in the following section because there are essential delays with different timescales. In the beginning of the nuclear tests, the radiocarbon concentrations were at the natural level in the ocean and in the biosphere and therefore only very tiny amounts of radiocarbon returned back into the atmosphere. This also means that the deep ocean is the main sink for radiocarbon, because 80% of radiocarbon will recycle back from the biosphere in 60 years, the rest will stay for more than 250 years as estimated in the next section. The direct measurements show that

radiocarbon has almost totally disappeared from the atmosphere. This is evidence that the ocean can be a real sink, at least for labelled CO_2 fluxes.

An essential question is, whether the anthropogenic CO_2 is behaving in the same way as the radiocarbon? Both isotope fluxes were added into the atmosphere, where these fluxes created an anomaly. The anthropogenic CO_2 flux into the atmosphere started around 1750 when the burning of coal was started. Because this anthropogenic CO_2 flux started from nil, the behaviour of anthropogenic concentration in the atmosphere is similar to the radiocarbon behaviour. Therefore a conclusion can be drawn that the decay rate of anthropogenic CO_2 cannot be quicker than that of radiocarbon but the residence time of the anthropogenic CO_2 decay

process should be the same as the decay rate of ^{14}C .

Segalstadt [3] has carried out a survey consisting of 34 residence time studies, in which six different methods were applied. The average value is 7.6 years among the studies showing residence times from 2 to 15 years. All these studies were published before 1990 starting from 1957. Segalstadt [3] has properly referred to eight papers. One common feature seems to be that the results are not based only on the direct measurements but a model has also been applied in calculating the residence times. A rather amazing thing is that 12 of these referred papers have used radiocarbon measurements in getting the residence times from 2 years to 12.5 years. The spread of the results also show that these results are not reliable. The author's conclusion is that the radiocarbon decay observation rate from 1964 to the present day without any models as depicted in Fig. 1 is so reliable that the results shorter than about 16 years residence time cannot be correctly calculated or evaluated. These results of a short residence time above contain also another serious common source of error, because they are usually addressed to be applicable to the total CO_2 decay rate in the atmosphere.

Sometimes the residence time or the time constant T of 4 to 5 years has been explained by a simple calculation of T by dividing the atmospheric mass with the average total recycling flux. Using the recycling fluxes values for the year 2013 in Table 2 and the measured CO_2 concentration in calculating the atmospheric CO_2 mass, T would be

$$T = \text{CIA} / (\text{FO}_{\text{dn}} + \text{FB}_{\text{dn}}) = 845 \text{ GtC} / (87 \text{ GtC yr}^{-1} + 123 \text{ Gt C yr}^{-1}) \sim 4 \text{ yr} \quad (1)$$

This calculation basis could be justified, if the atmosphere would be the only reservoir acting like a mixing chamber. But the atmosphere is only one element in the combination of four reservoirs with great recycling fluxes between three of them according to Fig. 1. Therefore this calculation basis is not correct for any of the CO_2 fluxes. This calculation is also based on the assumption that there is a constant flow through the mixing chamber, which is not true in this case. There is no chemical reaction going on in the atmosphere but the only physical process is an effective mixing. The addition of the annual fossil fuel emission flux is mixed during one year with the existing amount of the atmospheric CO_2 .

Actually the seasonal changes in the CO_2 concentration can be easily detected and therefore the yearly effects of the fossil fuel emissions can be noticed reliably after averaging the seasonal changes.

The recycling system of CO_2 comprising fluxes and reservoirs is rather complicated but the behaviour of this system can also be described with very simple formulas, which are applicable to the present day and probably for many years to come. The annual change rate of the atmospheric CO_2 mass CIA depends on the incoming fossil fuel emission rate F_{ff} and the outgoing flux into the ocean and into the biosphere F_{out} .

$$\Delta \text{CIA} = F_{\text{ff}} - F_{\text{out}}, \quad (2)$$

where $F_{\text{out}} = \text{FO}_{\text{up}} + \text{FB}_{\text{up}} - \text{FO}_{\text{dn}} - \text{FB}_{\text{dn}}$. The behaviour of the CIA change rate can be calculated with a simple linear formula,

$$F_{\text{out}} = K_{\text{out}} * (\text{CIA} - \text{CIA}_{1750}), \quad (3)$$

where CIA_{1750} is the atmospheric CO_2 amount in the year 1750, which is 597 GtC. K_{out} is calculated based on the average increase of CIA from 1950 to 2013 (182 GtC) and the value is 0.01775 yr^{-1} . The measured atmospheric CO_2 concentrations [10] have been used in calculating the yearly CO_2 flux rates and the CO_2 amount according to the empirical eq. (2); the both variables are depicted in Fig. 3. The yearly fossil fuel emissions are depicted as a reference only [11].

There are great differences between the measured and the empirically calculated yearly CO_2 values but the overall development is quite accurate. The simplest explanation is that the sink rate into the deep sea is the controlling step and it is proportional to the CO_2 concentration of the surface ocean. This concentration is proportional to the concentration of CO_2 in the atmosphere through Henry's law. The absorption rate from the atmosphere to the ocean is dependent only on the atmospheric CO_2 concentration and the surface ocean temperature. Therefore the overall change rate follows very well the atmospheric CO_2 amount. Eq. (3) cannot explain the yearly changes, because there is no term depending on the ocean temperature. An even a simpler rule can be formulated indicating that about 55% of the annual fossil fuel emissions stay in the atmosphere and the other 45% is absorbed by the sink.

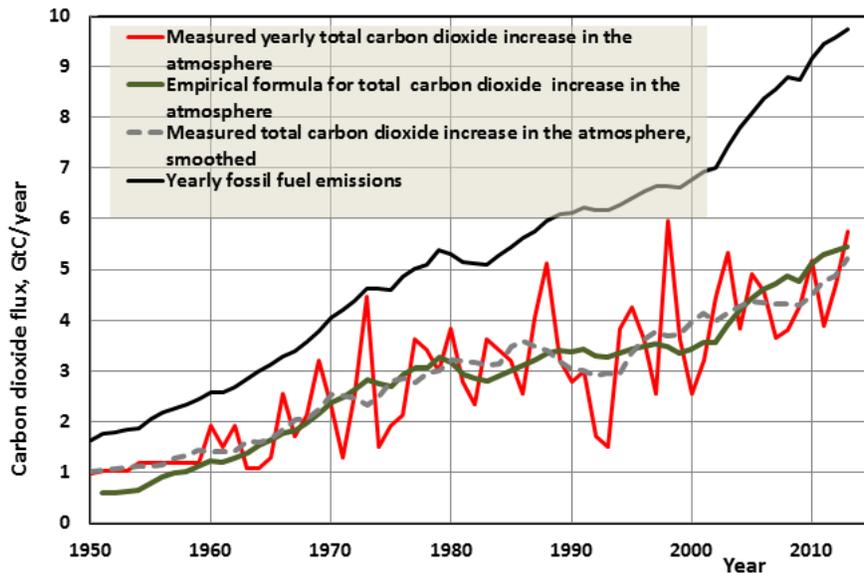


Fig. 3. The increase of the atmospheric CO₂ based on the linear empirical formula in comparison to the measured values

The atmosphere mixes the different CO₂ fluxes very effectively and quickly. The global ¹⁴C concentrations were globally evened after 4 years of nuclear tests. The maximum yearly CO₂ concentration difference is only about 4 ppm at the annual level between the South Pole and Mauna Loa [12]. The ideal mixing tank reacts on the input changes immediately. This effective mixing makes very sharp annual changes possible in the atmospheric CO₂ amounts. There are no reasons in the atmosphere, which could explain the annual concentration changes differentiating from the annual fossil fuel changes. Therefore the reasons originate from the recycling fluxes between the ocean and/or the biosphere. Ollila [1] has shown that there is a very strong correlation between the surface ocean temperature and the net CO₂ flux into the atmosphere.

The behaviour of the total CO₂ increase in the atmosphere behaves in a different way in comparison to radiocarbon and to the anthropogenic concentrations. The difference originates from the recycling fluxes of the ocean and from the biosphere back into the atmosphere. The recycling fluxes in and out between the reservoirs are essentially at the same level, which means that almost the same amounts of the total CO₂ is leaving and entering the atmosphere. Because there is only a minor dilution effect for the total CO₂, the residence time of the total CO₂ in the atmosphere must

essentially be longer than that of radiocarbon and anthropogenic CO₂. The dynamic delays depend on the flux rate F_{dep} into the deep ocean and the possible increase of the biosphere mass.

We can make a simple theoretical experiment. Let us think what would happen if the fossil fuel emissions of 10 GtC yr⁻¹ were stopped totally. What would happen to the F_{dn} and F_{bn} fluxes? We could expect that the average removal flux rate from the atmosphere during the next year would continue at about the present level, which would mean ~4.5 GtC yr⁻¹ (=45% from the 10 GtC yr⁻¹) in the next year. Thereafter the removal rate would gradually decrease. The ocean or the biosphere can react only on the concentration of the total atmospheric CO₂ amount.

What could be the first approximation of the adjustment time required that the atmospheric CO₂ concentration would come back to the CO₂ concentration of 280 ppm? Actually the concentration would be a little bit higher in the long run. The atmospheric concentration of 280 ppm has been in balance with the CO₂ amount in the ocean in 1750. An estimate of the CO₂ in 1750 is 38000 GtC. Using the relationship of (280 ppm / 38000 GtC) would mean a new balance value of 283 ppm of CO₂ in the atmosphere. The first rough adjustment time approximation would be the same time as required to get the present concentration of about 400 ppm, which would be 2016 – 1750 =

266 years. This calculation is based on the assumption that the ocean has a capacity to absorb the rest of the present “extra” atmospheric mass 256 GtC in 2015 (854 GtC – 597 GtC).

There are research studies showing the residence times around 200 years. O’Neill et al. [2] have calculated the residence time of 70 years making the adjustment time of about 175 years. Lashof and Ahuja [13] have estimated the adjustment time to be about 230 years. The residence time of 7.5 years would mean that the present amount of 854 GtC of the total CO₂ should come to 597 GtC during the adjustment time of $4 \times 7.5 = 30$ years. It would mean the linear decay rate of 29 GtC yr⁻¹, which is impossible.

IPCC has taken another “extreme” approach into the question of the anthropogenic CO₂ residence times in the atmosphere, when compared to the residence time of 7.5 years only. In AR4 IPCC applied the Bern model [14], which states that there are three residence times of 1.2, 18.5 and 173 years, and about 22% of any CO₂ input will stay in the atmosphere. In AR5 there is no specific lifetime formula. According to the IPCC [15] calculation method, after 2000 thousand years, the atmosphere will still contain between 15% and 40% of those initial emissions. This feature can be clearly seen in the RCP simulations, which show that the atmospheric CO₂ concentrations do not start to decrease even though the emissions decrease.

It may look like that there is a great conflict that the annual flux changes entering or leaving the atmosphere can be detected right away even as sharp annual peaks, and on the other hand that the long residence time of 16 years or even 70 years should smoothen these kind of changes almost totally. What is the physical explanation? There is no conflict. The mixing chamber’s essential feature is to mix any changes into easily detectable changes very quickly (theoretically immediately). If there is a step change, the change will happen immediately but the decay rate of the step change may be very long depending on the time constant of the process. The mixing capability of the atmosphere explains the sharp changes in the atmospheric CO₂ concentration but the recycling fluxes and the delays in the other reservoirs explain the long residence time of the system. This means that the total flush rate from the atmosphere $FO_{dn} + FB_{dn}$ is not the flux rate removing the total CO₂ into the sink (as assumed in the residence time

of 4 years only). The removing rate is controlled by the flux from the surface ocean into the deep sea.

3. THE EVALUATION OF THE OCEANIC AND LAND SINKS

There is a great uncertainty concerning the sizes of oceanic and land sinks/sources. The size of the atmospheric CO₂ amount is the most reliable figure due to the modern measurements technology. The anthropogenic amount of CO₂ in the ocean can be calculated with fairly accuracy utilizing the carbon isotope measurements. The terrestrial anthropogenic CO₂ source/sink evaluation cannot be measured directly and therefore it has normally been estimated as a difference between the anthropogenic CO₂ emissions and the atmospheric increase and oceanic sink.

The researchers have utilized different model based methods for the oceanic uptake of the total CO₂, and all of them show results which are usually close to each other. The box diffusion model [16] shows the oceanic uptake rate 1.9 ± 0.4 GtC yr⁻¹ from 1970 to 1990. The wind speed dependence of the CO₂ gas transfer velocity [17] shows the uptake rate 2.2 ± 0.4 GtC yr⁻¹ in 1995. The complicated global ocean general circulation models show the uptake rate 2.3 GtC yr⁻¹ from 1990 to 2007 [18] and 2.2 ± 0.3 GtC yr⁻¹ from 1995 to 2000 [19].

There are also studies based essentially on the carbon isotope tracer measurement methods in calculating the inventory estimates of the anthropogenic CO₂ inventory and uptake rates. Sabine et al. [20] has found that the global oceanic anthropogenic CO₂ sink from the period of 1800 to 1994 is 118 ± 19 GtC, Waugh’s et al. [21] estimate 134 GtC is from the same period, and Khatiwala’s [22] for the inventory is 140 ± 25 GtC in 2008 leading to the uptake rate of 2.3 ± 0.6 GtC yr⁻¹. Sabine and Tanhua [23] have summarized that the most common estimate of the oceanic anthropogenic CO₂ inventory in the mid of 1990 is about 120 GtC.

There is also a method, which utilises the O₂/N₂ ratio and atmospheric CO₂ concentration measurements in calculating the oceanic and land sink sizes. Manning & Keeling [24] have calculated that from the period of 1990 to 2000 the oceanic uptake rate was 1.71 ± 0.52 GtC yr⁻¹ and the land sink rate was 1.41 ± 0.66 GtCyr⁻¹ but the uptake rates from 1993 to 2003 were 2.2 ± 0.6

GtC yr⁻¹ and 0.51±0.74 GtC yr⁻¹ respectively. These results show that the land uptake rate has increased 0.7 GtC yr⁻¹ in only three years. Sarmiento and Gruber [25] have reported that in the 1980s the oceanic uptake rate was 1.9±0.6 GtC yr⁻¹ and the net land uptake was 0.2±0.7 GtC yr⁻¹. The oceanic/land ratio sink according to this example would be about 9/1. This means that either this method is not accurate enough as seen in the large uncertainty values or the uptake rates fluctuate strongly on a yearly basis and also regionally, which has been proposed [26].

The majority of the studies as referred above concerning the sinks show that the division between the ocean and the land is about equally distributed but there are other results as well. Sabine et al. [20] has estimated that the terrestrial biosphere has been the net source of 38±28 GtC for the period between 1880 and 1994. Khatiwala et al. [22] has estimated that the land has been a net source of CO₂ during the industrial period (1750-2008) from neutral to as much as half has been taken up by the ocean.

In AR5 [15] is a conclusion that in 2011 the amount of accumulated anthropogenic CO₂ in the atmosphere is total 240 GtC. Some researchers [25] make the same assumption. This assumption means that the ocean would have a capability to select the molecules in the absorbing process but there is no evidence of this. There are direct δ¹³C measurements in the atmosphere, which show that the present δ¹³C value is about -8.4‰. According to Ollila [1] this means the amount of 67 GtC anthropogenic CO₂ in the atmosphere and the amount of 240 GtC anthropogenic CO₂ would mean a δ¹³C value of -12.9‰. It seems that the researchers do not always make a difference between the total CO₂ and the anthropogenic CO₂ amounts and fluxes but this should be taken into account in calculations [24].

There are two main schools of thoughts concerning the oceanic uptake process. The most common approach could be called "a buffer factor" based estimation. The buffer factor means a buffering of CO₂ is exchanged from air to seawater, and it is also known as the "Revelle factor" [27]. This approach leads to the net dissolving rate of about 2-3 GtC yr⁻¹ [13], which is not essentially dependent on the increasing atmospheric CO₂ concentration of today because of the buffering phenomenon. The oceanic uptake rates of the referred studies above are in line with this approach.

The most general approach of the sizes of sinks leads into the "missing sink" problem [28]. During the years of 2013 to 2015 the fossil fuel emissions have been at the level [11] about 10 GtC yr⁻¹ and the atmospheric CO₂ increase has been about 5.5 GtC yr⁻¹ leading to the sink rate about 4.5 GtC yr⁻¹. If the ocean sink rate is about 2.2 GtC yr⁻¹, then the land sink rate would be about 2.3 GtC yr⁻¹. This approach suggests that the biosphere is the missing sink. There is no direct evidence of this and thinking the deforestation problem for example, this is not very likely, but the greening of the Earth is a supporting factor. There is also a possibility that the contraction of rain forest areas has decreased the biomass more than the greening of dry areas. The continuation of the present situation weakens the Revelle factor's approach as explanation for the deep ocean sink rate. New research studies utilising the same methodology as used by Sabine et al. [20] are needed to find out what is the real oceanic inventory of the anthropogenic CO₂.

There is also an approach, which does not accept the almost constant buffer capacity of the ocean. Ollila [1] has a summary about these studies, which show that the ocean may have an infinite buffer capacity [29]. In this paper this approach has been applied.

The continuously rising CO₂ concentration started in 1750 and now looks like that the increase rate of fossil fuel emissions has evened out to the level of about 10 GtC yr⁻¹. If the theory according to equations (2) and (3) is applied, the increase of the CO₂ concentration should continue with the current average rate of about 2.2 ppm yr⁻¹. If this rate decreases, it is a sign of the change of the controlling process step of the deep ocean absorbing rate. The atmosphere has been in a dynamic change condition for about 260 years. The effects of this change are in the system and an annual increase of the fossil fuel emissions is actually a very small change in comparison to the total effect already in the system.

4. DESCRIPTION OF THE ENHANCED 1DAOBM-2

In this section the enhancements included in the original 1DAOBM has been described. The modified model has been named 1DAOBM-2.

The 1DAOBM-2 is based on the following assumptions: 1) the anthropogenic and natural

CO₂ are fully mixed in the atmosphere, 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, 7) the cumulative flux rates from 1750 to 2013 between the reservoirs are adjusted to fulfil the mass balance requirements.

The theoretical bases of these choices are explained in the original paper of Ollila [1]. The most important choice is that there is no missing sink of carbon. It is assumed that the ocean can continue to absorbing also 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-2 this part is represented by the empirical linear first order equation. The DIC values can be calculated as functions of CO₂ and sea water temperature according to equations (5) and (6) [1]:

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

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

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

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

In these equations DIC is dissolved inorganic carbon (mol/t), T is temperature (°C) [30], and C is CO₂ concentration (ppm) [31]. The reference [31] includes the values of the ice core measurements starting from 1832, which have been smoothed for 20 years. The author has applied the linear increase from the value of 280 ppm in 1750 to 286.4 ppm in 1840. The CO₂ concentrations from 1959 onward are based on the Mauna Loa values.

In Table 2 the formulas and numerical values of 1DAOBM-2 are depicted.

The modifications of formulas applied in 1DAOBM-2 are shortly explained. The starting value of FO_{tot,dn} and FO_{tot,up} in 1750 are 80.5 GtC/y, which are 19.5 GtC/y smaller than in 1DAOBM. In 2011 FO_{tot,dn} is 87.0 GtC/y, which about 10% greater than the value used by IPCC [13].

The flux value of FB_{tot,up} is still based mainly on the results of the reference [15] but the portions of different turnover times are applied in eq. (16). 55 percentage portion of the total CO₂ assimilated by the biosphere is respired back by the plants in a year, 12.5% will recycle back from the detritus after a turnover time of 7 years, and 12.5% in 15 years. The rest 20% of CO₂ is converted into soil organic carbon and its turnover time varies a lot even up to 1000 years depending on the source. In 1DAOBM-2 a turnover time of 250 years has been applied for 15% of FB_{tot,up} flux. The rest 5% of soil organic carbon will not recycle back into the atmosphere.

A major empirical parameter in these simulations is parameter K_{ant} in eq. (19), which is used in calculating the flux F_{ant,deep}. The value of 17.5 is selected so that the global anthropogenic δ¹³C in the atmosphere in 2013 is -8.4‰, which is equal to 67 GtC [1]. Eq. (19) has been modified in this model to have two driving elements for the F_{ant,deep} flux namely the total CO₂ concentration difference multiplied by the portion of anthropogenic CO₂ in respect to the total CO₂.

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 [28]. The regional conditions of the surface ocean may vary but in the global scale the CSO_{tot} amount controls the F_{tot,deep} flux into the deep ocean.

In this model the ocean has a major role in explaining the anthropogenic and total CO₂ concentration changes in the atmosphere. In 1DAOBM-2 there are no adjustable constants in calculating the net CO₂ flux F_{A,net} into the atmosphere according to eq. (21) from 1956 onward. In the same way also the net natural CO₂ natural flux F_{A,nat} from the ocean into the atmosphere is calculated according to eq. (22) by a direct physical relationship. The total atmospheric change of 248 GtC is the sum of natural CO₂ from the ocean 181 GtC and the anthropogenic CO₂ 67 GtC.

The calculation of the total CO₂ flux rate from the atmosphere into the ocean and into the biosphere is demanding, because there are no direct measurements supporting the formulation of the equations. An important discovery is illustrated in Fig. 4 in which has

Table 2. The calculation bases for variables in the 1DAOBM-2 simulations. The differences in respect to 1DAOBM are written by italic font. The amounts are in GtC and fluxes are in GtC yr⁻¹. The main fluxes are introduced in Fig. 1

Variable acronym	Variable name	Calculation formula
FO _{tot,dn}	Total dissolution carbon pump flux from the atmosphere into the ocean	$80.5 + K_{dn} * F_{ff}$; $K_{dn} = 0.685$ (6)
FLUSH _{AO} -%	Flush-% of the dissolution pump from the atmosphere into the ocean	$100 * FO_{tot,dn} / CIA_{tot,n}$ (7)
FO _{ant,dn}	Anthropogenic dissolution carbon pump flux from the atmosphere into the ocean	$FLUSH_{AO}\% * CIA_{ant,n-1} / 100$ (8)
FO _{tot,up}	Total dissolution carbon pump flux from the ocean into the atmosphere	$80.5 + K_{up} * F_{ff}$; $K_{up} = 0.463$ (9)
FLUSH _{OA} -%	Flush-% of the dissolution pump from the ocean into the atmosphere	$100 * FO_{tot,up} / CSO_{tot,n}$ (10)
FO _{ant,up}	Anthropogenic dissolution carbon pump flux from the ocean into the atmosphere	$FLUSH_{OA}\% * CSO_{ant,n-1} / 100$ (11)
FB _{tot,dn}	Total biosphere carbon cycle flux from the atmosphere into the biosphere	123 (12)
FB _{tot,up}	Total biosphere carbon cycle flux from the biosphere into the atmosphere	121.6 (13)
FLUSH _{AB} -%	Flush-% of the biosphere carbon cycle from the atmosphere into the biosphere	$100 * FB_{tot,dn} / CIA_{tot,n}$ (14)
FB _{ant,dn}	Anthropogenic biosphere carbon cycle flux from the atmosphere into the biosphere	$FLUSH_{AB}\% * CIA_{ant,n-1} / 100$ (15)
FB _{ant,up}	Anthropogenic biosphere carbon cycle flux from the biosphere into the atmosphere	$0.9891734 * (0.55 * FB_{ant,dn,n} + 0.125 * FB_{ant,dn,n-7} + 0.125 * FB_{ant,down,n-15} + 0.15 * FB_{ant,down,n-250})$ (16)
FN _{tot,deep}	Net total CO ₂ flux from the surface ocean into the intermediate & deep ocean	$K_{tot} * (CSO_{tot,n} - CSO_{ref})$; $K_{tot} = 0.169$; $CSO_{ref} = CSO_{1750}$ (17)
FN _{tot,ocean}	Net total CO ₂ flux into the ocean	$FN_{tot,deep} + \Delta CSO_{tot}$ (18)
FN _{ant,deep}	Anthropogenic net CO ₂ flux from the surface ocean into the intermediate & deep ocean	$K_{ant} * (CSO_{tot,n} - CSO_{ref}) * (CSO_{ant} / CSO_{tot,n})$; $K_{ant} = 17.5$; $CSO_{ref} = CSO_{1750}$ (19)
FN _{ant,ocean}	Net anthropogenic CO ₂ flux into the ocean	$FN_{ant,deep} + \Delta CSO_{ant}$ (20)
F _{A,net}	Net CO ₂ (natural + anthropogenic) flux into the atmosphere	$F_{ff} - FN_{tot,ocean}$ (21)
F _{A,nat}	Net natural CO ₂ flux from the ocean into the atmosphere	$F_{A,net} - \Delta CIA_{ant}$ (22)
ΔCSO _{ant}	Anthropogenic CO ₂ change in the surface ocean	$FO_{ant,down} - FO_{ant,up} - F_{ant,deep}$ (23)
ΔCDO _{ant}	Anthrop. CO ₂ change in the deep ocean	$F_{deep,n} - F_{deep,n-1}$ (24)
ΔCIB _{ant}	Anthrop. CO ₂ change in the biosphere	$FB_{ant,down} - FB_{ant,up}$ (25)
ΔCIA _{ant}	Anthrop. CO ₂ change in the atmosphere	$F_{ff} + \Delta CDO_{ant} + \Delta CIB_{ant}$ (26)
CSO _{tot}	Total CO ₂ in the surface ocean	Equations (1) and (2)

been depicted the cumulative increase of CO₂ in the atmosphere [31] and the cumulative fossil fuel emissions [11] starting from the year 1750. The year 1956 is the first time when the cumulative value of the atmospheric CO₂ increase was greater than that of the total fossil fuel emissions. It means that the ocean and/or land have been a net source of CO₂ up to 1956.

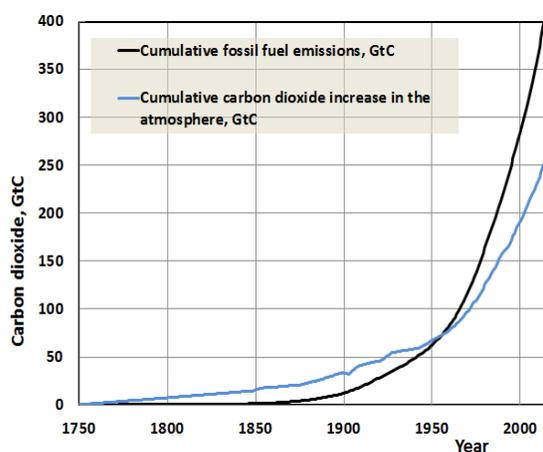


Fig. 4. The cumulative fossil fuel emissions and the cumulative CO₂ increase in the atmosphere from 1750 to 2015

The logical steps in developing the formulas and the constants included are depicted in Table 3.

The fossil fuel emission rates F_{ff} as well as the atmospheric CO₂ amounts are based on the measurements. The anthropogenic ΔCIA_{ant} amounts are calculated using the 1DAOBM-2. It has been assumed that ΔCIA_{tot} is the sum of ΔCIA_{ant} and natural CO₂ from the ocean $\Delta CIA_{nat, ocean}$ and therefore $\Delta CIA_{nat, ocean}$ values are simple to calculate. The flux changes from the biosphere have practically no effects on the atmospheric CO₂ composition, because the fluxes in

and out of the biosphere have the same $\delta^{13}C$ values.

The net total CO₂ flux into the deep ocean $FN_{tot, deep}$ is calculated by eq. (17) and it is a linear relationship between the yearly CO₂ concentration in the surface ocean (CSO) and the total CO₂ concentration in the year 1750. The value of coefficient K_{tot} is 0.169 and it has been adjusted to get the cumulative sum of 146 GtC into the ocean from 1956 to 2013. This is based on the assumption that during this time period the ocean is the only sink for the total CO₂. The ΔCIB_{tot} values can be calculated as differences between the total sink values and the sink values into the ocean. The final results of these calculations are that from 1750 to 1956 the biosphere has been the sink of 59 GtC and the ocean has been the source with the same amount. During the period from 1750 to 2013 the biosphere's sink value is 59 GtC and the ocean's sink value is 87 GtC with a total of being 146 GtC. This means that the division of the sink between the ocean and the biosphere is 60% versus 40%.

The coefficient K_{dn} in eq. (6) is selected to adjust the cumulative increase of $FO_{tot, dn}$ from 1750 to 2013 to be 350 GtC. The coefficient K_{up} in eq. (9) is adjusted to increase the cumulative change of $FO_{tot, up}$ from 1750 to 2013 to be 263 GtC resulting into the net cumulative flux rate change $(\Delta CSO + \Delta CDO)_{tot}$ 87 GtC from the atmosphere into the ocean. The flux value of $FB_{tot, dn}$ is 123 GtC/y as used by IPCC [15], and $FB_{tot, up}$ is 121.6 resulting into the cumulative sink value of 59 GtC from 1750 to 2013. There is a 12 month time delay between the ocean temperature change and the outgassing of CO₂ into the atmosphere.

The total CO₂ sink rate change from 1730 to 2013 into the ocean and into the biosphere is 146 GtC (= 394 GtC – (845 GtC – 597 GtC)) and it depends on the small annual changes between the atmosphere, the ocean and biosphere.

Table 3. The CO₂ flux rates and reservoir value changes of the atmosphere, the ocean and the biosphere from 1750 to 2013

Flux (GtC yr ⁻¹) or reservoir (GtC)	1750 – 1956	1956 - 2013	1750 - 2013
Fossil fuel emission, F_{ff}	72	322	394
Atmosphere, ΔCIA_{tot}	72	176	248
Atmosphere, ΔCIA_{ant}	13	54	67
Atmosphere $\Delta CIA_{nat, ocean}$	59	122	181
Ocean, $(\Delta CSO + \Delta CDO)_{tot}$	-59	146	87
Ocean, $(\Delta CSO + \Delta CDO)_{ant}$	34	177	211
Biosphere, ΔCIB_{tot}	59	0	59
Biosphere, ΔCIB_{ant}	25	91	116

The process controlling steps are the flux rate into the deep ocean and the mass changes of the biosphere. These changes are also related to the cumulative changes of recycling flux rates between these reservoirs. The anthropogenic CO₂ is flushed from the atmosphere into the ocean and into the biosphere by the recycling fluxes. This flushing happens even though the recycling flux rates would fluctuate or even decrease. That is why the anthropogenic sink values of the ocean and the biosphere are greater than the sink values of the total CO₂.

The cumulative values of different fluxes as well as the reservoir changes from 1750 to 2013 are depicted in Fig. 5.

There is a mass balance between the reservoirs. The only exception is in the flux rates of the natural CO₂ flux between the atmosphere and the ocean.

5. RESULTS AND DISCUSSION

The main objective of this study is to find the different residence times of 1DAOBM-2, because it is a way to compare the results with the theoretical analyses and with the other models. The easiest way is to make a simulation, in which the fossil fuel emission is forced into zero level, because then a first order dynamic model can be easily fitted. The author has selected the year

1964 for this change, because it is the same year when the nuclear tests were stopped. The results are depicted in Fig. 6.

The decay rate of anthropogenic CO₂ in the atmosphere is depicted with the brown graph. The residence time of 16 years gives a very good result. It is exactly the residence time as measured for ¹⁴C decay rate.

The decay rate of the total atmospheric CO₂ concentration calculated by 1DAOBM-2 is depicted with the green graph. This graph is calculated to 2140 applying the eq. (17), where CSO_{ref} is 704.4 GtC. Thereafter the CSO_{ref} is linearly growing to the value of 704.9 GtC, which brings the CO₂ concentration to the value of 280.8 ppm. This is the balance value between the atmosphere, the surface ocean and the deep ocean, when totally 91.5 GtC of fossil fuels have been released into the atmosphere.

The black dashed graph is the fitting with the residence time of 55 years, which gives only slightly lower values in the middle part of the change. There are two graphs depicted as references. The blue dashed line is the decay rate according to the Bern model [12]. It gives in the beginning of the change much lower values than 1DAOBM-2 and in the end it stays at the level of 290.5 ppm. The final balance value would be 280+0.217*39 ppm = 288.5 ppm.

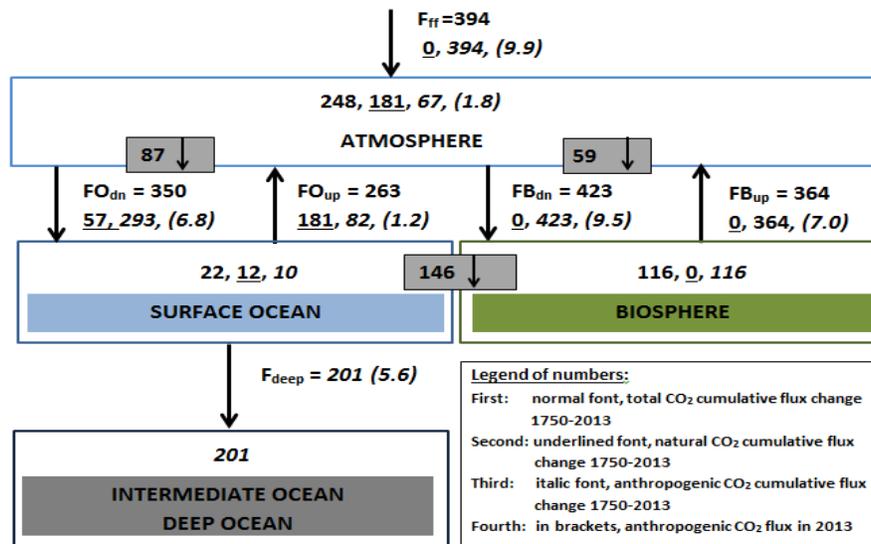


Fig. 5. The cumulative flux CO₂ flux changes values the between the reservoirs from 1750 to 2013, and cumulative changes of reservoirs from 1750 to 2013

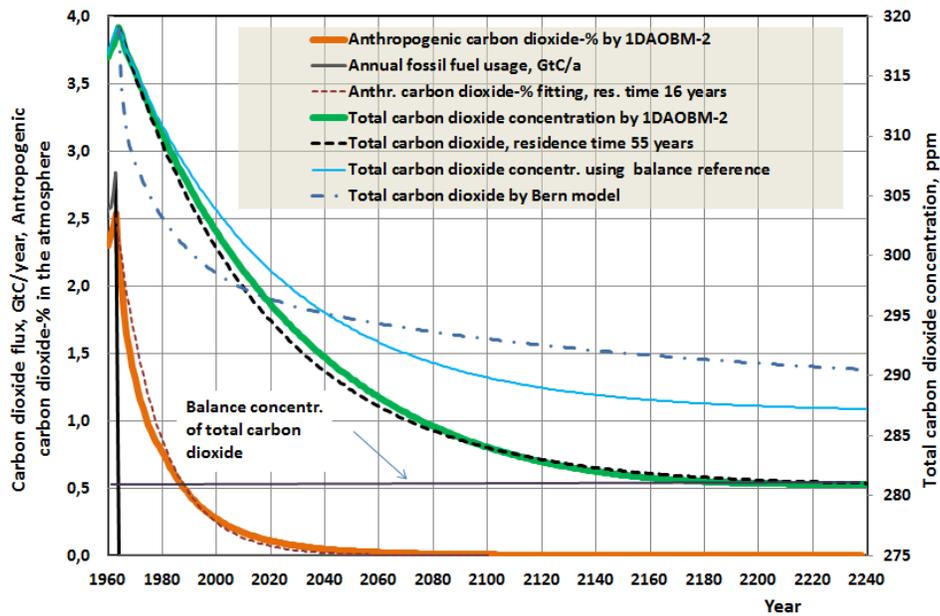


Fig. 6. The simulated results of the fossil fuel change to zero GtC yr^{-1} in 1964 onward

The blue line represents the result calculated by 1DAOBM-2 utilising the balance value of CSO_{ref} instead of the constant 704.4 GtC. This choice means that CSO_{ref} increases to 707.4 GtC and therefore the driving force into the deep sea decreases gradually in comparison to the constant CSO value. The CO_2 concentration comes to the level of 287 ppm, which is close to the value of the Bern model. Using the balance CSO value as a reference might be justified, because the CO_2 amount in the deep ocean should not go over the balance value. On the other hand it looks like that in the early phases of the deep sea absorption, the diffusion rate into deep sea is dependent on the constant value of CSO_{1750} only as it has happened since 1956. Sabine et al. [18] have estimated that in 1994 only 30% of the deep sea absorption capacity was utilized.

Climate models are constructed first of all to simulate atmospheric CO_2 concentrations of the future and future temperature changes. 1DAOBM-2 is designed to simulate the CO_2 concentrations but the effects of the temperature changes can be included only indirectly. One possible future scenario of the fossil fuel emissions is that they stay at the same level as they have been now three years namely 10 GtC yr^{-1} and this was simulated by 1DAOBM. The results of this simulation by 1DAOBM-2 are almost similar to the original 1DAOBM

simulation. The CO_2 concentration increases steadily up to about 700 ppm in 2300. The only difference is in the behaviour of anthropogenic CO_2 -% in the atmosphere, which is levelling off to 9.3% (8.0% in 2013) after the adjustment time of about 64 years (year 2080).

Another possible scenario is the RCP4.5 projection specified by IPCC [32]. In this projection the fossil fuel emission reach the maximum of 11.5 GtC yr^{-1} in 2030. The results are depicted in Fig. 7.

The CO_2 concentration of 1DAOBM-2 behaves in a different way in comparison to the RCP4.5 simulation by IPCC. The essential difference is that according to the IPCC the anthropogenic CO_2 of the present atmosphere cannot be flushed into any sink. The total CO_2 will increase to 538 ppm and it will stay there for centuries. According to the 1DAOBM-2 model, the total CO_2 concentration starts to gradually decrease in 2060 and will come finally to the balance value. These results are close to the results carried out by 1DAOBM except the behaviour of anthropogenic CO_2 , which descends now smoothly after the maximum value in 2040.

Even though 1DAOBM-2 is semi-empirical, there are some results of the model, which can be used for validation of the model. The amount of

the observed anthropogenic CO₂ quantities in the ocean from 1750 to 1994 is 118±19 GtC [18] and according 1DAOBM-2 calculations it is 122.7 GtC, which is only 4% greater and well inside of the uncertainty limits. The residence time of the anthropogenic CO₂ decay rate is the same 16 years as measured in the ¹⁴C decay rate and,

according to theoretical analysis, they should be the same.

1DAOBM-2 can be applied to simulate the fluxes and CO₂ concentrations from 1750 to 2013 using the measured atmospheric CO₂ concentrations. The results from 1950 to 2013 are depicted in Fig. 8.

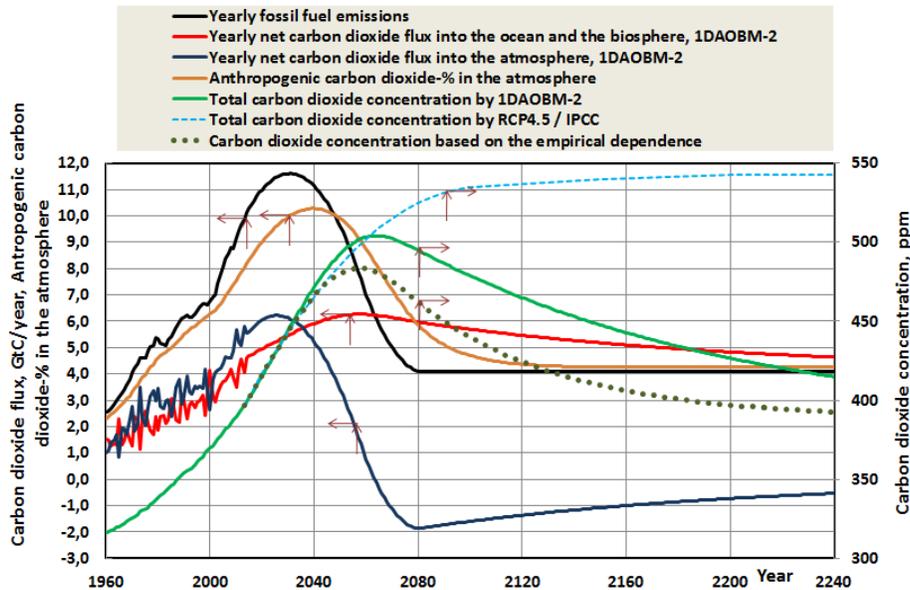


Fig. 7. The simulation results of the projection RCP4.5

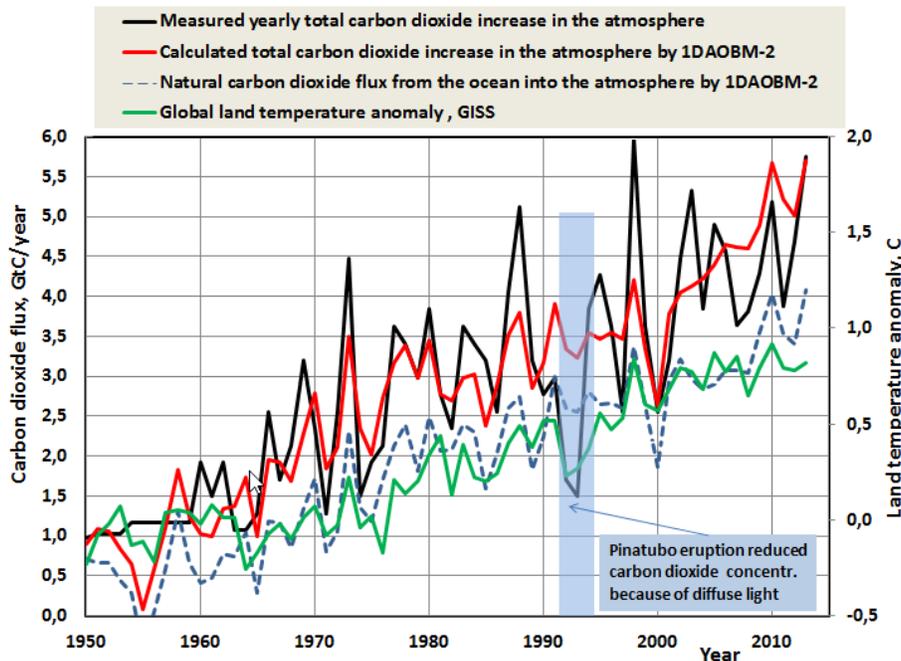


Fig. 8. The simulated fluxes from 1950 to 2013

The essential feature is the calculated net flux of the total CO₂ into the atmosphere. This flux includes not only the fuel emissions but also the recycling fluxes between the atmosphere and the ocean as well as the recycling fluxes between the atmosphere and the biosphere. The black graph is the atmospheric CO₂ concentration flux and the red graph is the flux calculated by 1DAOBM-2. The model produced flux follows very well the observed yearly flux variations. The coefficient of correlation r^2 is 0.76 for this period. When the years of the Mt. Pinatubo eruption from 1991 to 1995 are excluded from the data, the r^2 is 0.81. During the Mt. Pinatubo eruption the plants could photosynthesize more effectively in the diffuse sunlight and therefore there is an anomaly downwards in the CO₂ concentration [33].

The blue trend on the graph is the natural CO₂ flux from the ocean into the atmosphere. The cumulative value of this flux from 1750 to 2013 is 181 GtC. Together with the anthropogenic CO₂ amount 67 GtC in the atmosphere this flux explains the total 248 GtC increase from 597 GtC in 1850 to 845 GtC in 2013. In a way this result is a piece of good news for those 34 research studies, which have been surveyed and detailed in the reference [3], who claim that the total CO₂ increase in the atmosphere originates totally from the ocean, because according to 1DAOBM-2 model the portion of natural CO₂ from the ocean is 73% in the present atmosphere. At the same time this is a piece of bad news for these researchers, because the original reason for the CO₂ increase in the atmosphere is 100% due to the fossil fuel emissions.

According to those researchers, who show the deep ocean rate of about 2.2 GtC yr⁻¹, the biosphere could be as great a sink as the ocean. If this would be the case, then the atmospheric CO₂ concentration changes should correlate to the land temperature changes. IPCC [15] refers to the research results that show that the annual CO₂ to be mainly driven by terrestrial processes occurring in tropical latitudes. Levels of carbon dioxide in the atmosphere increase and decrease on a yearly basis as plants, through photosynthesis and respiration, take up CO₂ in spring and summer, and release it during fall and winter. Fluctuations of about ±4 ppm can be clearly observed in the global CO₂ concentration curve [10]. They are caused by the seasonal photosynthesis rate variations, because the mass of the biosphere is large on the northern hemisphere. The research studies [34,35] show

that the photosynthesis rate of C3 and C4 plants increases as the temperature goes up. Therefore higher land temperature causes higher photosynthesis rate and it decreases the CO₂ concentration in the atmosphere.

In Fig. 8 is depicted also the land temperature. It is easy to compare the ups and downs of the CO₂ concentration variations and the land temperature variations. It is very clear that these curves match together and the coefficient of correlation r^2 is 0.71. Because higher land temperature should increase the photosynthesis rate and cause lower CO₂ in the atmosphere, this result does not support the theory that the fluctuations of the absorption rate of the biosphere could explain the annual changes of the atmospheric CO₂ concentration. The correlation between the sea temperature and the atmospheric CO₂ yearly fluctuations include the physical dependence between these variables but in the case of the land temperature changes, the physical dependence is negative.

In the future projection calculations 1DAOBM-2 cannot use the measured CO₂ concentrations. Based on the fossil fuel emissions 1DAOBM-2 calculates the CO₂ fluxes between the reservoirs and finally the CO₂ concentration. If this concentration does not match with the default value, the calculations can be continued by iteration method until the CO₂ concentrations are the same. One validation test was carried out starting from 1960 to 2013 using only the annual fossil fuel emission rates. The total CO₂ concentration by this validation test was 396.72 ppm. This difference between the measured value of 396.50 ppm is 0.22 ppm resulting to the error of 0.2% only.

There are no measured values for the total CO₂ residence time. The residence time T value of 1DAOBM-2 is 55 years resulting to 220 years adjustment time T_{adj} . Because 1DAOBM-2 simulates accurately the anthropogenic CO₂ residence time T , it is a positive signal, that it could simulate accurately also the total CO₂ decay rate. The accuracy of 1DAOBM-2 model depends strongly on the deep sea diffusion rate. As long as it is capable to absorb the atmospheric CO₂ at the present rate, 1DAOBM-2 describes the CO₂ fluxes in the right way as it has done from 1750 to 2015.

Ollila [1] had identified in the earlier study the residence times from the differences between the peak value of the emission rate F_{ff} and the peak

values of CO₂ concentration changes. This method is applicable for the plug flow reactor type process but not good enough for the process containing mixed tank type process. Therefore the residence time results for the total CO₂ are longer in this study.

In Fig. 9 is depicted the δ¹³C or permille values based on 1DAOBM-2 and the measurement graph is combined from the two measurements: from 1750 to 1980 [36] and from 1980 to 2013 [37]. The model based values are calculated applying the formula,

$$\delta^{13}\text{C} = \frac{(\text{CIA}_{\text{ant}} * (-28) + (\text{CIA}_{\text{tot}} - \text{CIA}_{1750} - \text{CIA}_{\text{ant}}) * (-8) + \text{CIA}_{1750} * (-6.35))}{\text{CIA}_{\text{tot}}} \quad (27)$$

The present atmosphere is the mixture of three CO₂ fractions: the anthropogenic amount, the fraction originating from the ocean, and the atmospheric mass in 1750. The permille values of these fractions are: the fossil fuel CO₂ -28‰, the ocean -8‰, and the atmosphere in 1750 -6.35‰ [36]. The average permille value of the surface ocean is about from +1.2‰ to +1.6‰ [5]. There is a slight fractionation, when CO₂ passes through the air/sea interface. Inoue and Sugimura [38] have estimated that air to sea value is about -10‰ and the sea to air value is -8‰. Therefore the value -8‰ has been used in eq. (27). The results show that the permille values of the 1DAOBM-2 model and the eq. (27) are very close to the observed values in the atmosphere. This result supports the sink and source values as presented in Table 3.

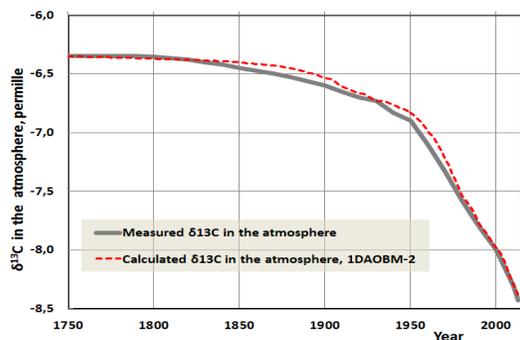


Fig. 9. The δ¹³C values according to the direct measurements and 1DAOBM-2

As far as more complicated methods are concerned, they cannot show a trustworthy method for calculating the missing sink reservoir, simple models like the 1DAOBM-2 developed in this study can be used to simulate atmosphere–

ocean fluxes, which corresponds the observations with very good accuracy.

6. CONCLUSION

The 1DAOBM-2 model gives results which follow very well with the observations. The validation of any model is necessary. There are four simulations results, which have been used for validation: 1) The amount of the observed quantities of anthropogenic CO₂ in the ocean from 1750 to 1994 is 118±19 GtC [18] and according to 1DAOBM-2 calculations it is 122.7 GtC, which is only 4% greater and well inside of the uncertainty limits. 2) The anthropogenic CO₂ decay rate of the 1DAOBM-2 follows very accurately the observation based decay rate of radiocarbon ¹⁴C since the nuclear test ended in 1964 giving the residence time of 16 years. 3) A validation test was carried out starting from 1960 to 2013 using only the annual fossil fuel emission rates without utilizing the atmospheric CO₂ concentration measurements. The total CO₂ concentration from this validation test was 396.72 ppm. This difference between the measured value of 396.50 ppm is 0.22 ppm resulting in an error of only 0.2 %. 4) The results show that the atmospheric permille values of the 1DAOBM-2 model are very close to the observed values in the atmosphere. This result supports the sink and source values between the reservoirs as found in the analysis.

Because there are suggestions that the land temperature changes could explain the atmospheric CO₂ concentration changes, this relationship has been analysed. The analysis shows that the land temperature changes should cause the opposite effects than those found in CO₂ concentration changes. The correlation between the sea temperature and the atmospheric CO₂ yearly fluctuations include the physical dependence between these variables and it supports the relatively high coefficient of correlation r² = 0.81, when the Pinatubo anomaly has been removed.

1DAOBM-2 is evidence that the CO₂ transfer from the atmosphere into the ocean can be described with Henry's law. The absorbance dependence of Henry's law on the atmospheric CO₂ concentration and the oceanic temperature can explain both the anthropogenic CO₂ variations in the ocean and in the atmosphere. These results can explain the history. The future scenario calculations are based on the assumption that the deep sea diffusion rate

continues according to the same linear formula depending only on the CO₂ concentration in the surface ocean.

The results of 1DAOBM-2 show that the ocean is capable to uptake the entire CO₂ after the year 1956 not found in the atmosphere. This is not true with the anthropogenic CO₂ where the biosphere has an essential role.

The simulation calculations show that the anthropogenic fraction of CO₂ in the atmosphere in 2013 was only 8.0 %. This result is based on the diluting effect of the carbon cycle between the atmosphere, the ocean, and the biosphere. This result differs totally from IPCC's value of 28% [15], but it is close to real observations and [33,34]. This low fraction 8.0% of anthropogenic CO₂ explains extremely well the observed δ¹³C of -8.4‰ in the present atmosphere. There is almost a perfect match between the calculated and measured δ¹³C 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 δ¹³C.

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. 1 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.

The sink division between the ocean and the biosphere still remains unsure, because there are no direct measurements based methods to detect this matter. Anyway the cumulative mass balance of the atmospheric CO₂ amount and the cumulative fossil fuel emissions show that the ocean and/or biosphere turned from the net source to the net sink around the year 1956. The good correlation of the atmospheric CO₂ concentration to the ocean temperature as well as to the absorption capability of the ocean through Henry's law indicates that after 1956 the ocean has been the major sink.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Ollila A. Anthropogenic carbon dioxide (CO₂) amounts and fluxes between the atmosphere, the ocean and the biosphere. *Physical Science International Journal*. 2015;8(1):1-17.
2. O'Neill BC, Gaffin SR, Tubiello FN, Oppenheimer M. Reservoirs timescales for anthropogenic CO₂ in the atmosphere. *Tellus*. 1994;46B:378-389.
3. Segalstad TV. Carbon cycle modelling and the residence time of natural and anthropogenic atmospheric CO₂: On the construction of the "greenhouse effect global warming" dogma. The continuing debate, European Science and Environmental Forum (ESEF), Cambridge, England. 1998;184-219.
4. NOAA, The data: What ¹³C tells us. The global view. Available:<http://www.esrl.noaa.gov/gmd/outrreach/isotopes/c13tellsus.html> (Accessed 15 Feb 2016)
5. Locean. Oceans 13C. Available:<https://www.locean-ipsl.upmc.fr/oceans13c/indexAng.htm> (Accessed 15 Feb 2016)
6. Levin I, Naegler T, Kromer B, Diehl M, Francey RJ, Comez-Pelaez AJ, et al. Observations and modelling of the global distribution and long-term trend of atmospheric ¹⁴CO₂. *Tellus*. 2010;62B:26-46.
7. Universiteit Utrecht. Radiocarbon dating. Available:<http://web.science.uu.nl/AMS/Radioc> (Accessed 10 Feb 2016)
8. Lawrence Livermore National Laboratory. ¹⁴C "Bomb Pulse" Pulse Forensics. Available:<https://cams.llnl.gov/cams-competencies/forensics/14c-bomb-pulse-forensics> (Accessed 10 Feb 2016)
9. Essenhigh RE. Potential dependence of global warming on the residence time (RT) in the atmosphere of anthropogenically sourced carbon dioxide. *Energy & Fuels*. 2009;23:2773-2784.
10. NOAA. Global CO₂ data base. Available:ftp://afpp.cmdl.noaa.gov/products/trends/co2/co2_annmean_mlo.txt (Accessed 5 March 2015)
11. Carbon emission from 1750 to 2013. Available:http://cdiac.ornl.gov/ftp/ndp030/global.1751_2010.ems (Accessed 5 March 2015)

12. Scripps. Graphics gallery, Mauna Loa and South Pole difference.
Available:http://scrippsco2.ucsd.edu/graphics_gallery/mauna_loa_and_south_pole/mauna_loa_and_south_pole_difference
(Accessed 10 Feb 2016)
13. Lashof DA, Ahuja DR. Relative contributions of greenhouse gas emissions to global warming. *Nature*. 1990;344:529-531.
DOI: 10.1038/344529a0
14. IPCC Fourth Assessment Report (AR4). The physical science basis, contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change, Cambridge University Press, Cambridge; 2007.
15. IPCC Fifth Assessment Report (AR5). The physical science basis. working group I contribution to the IPCC fifth assessment report of the intergovernmental panel on climate change, Cambridge University Press, Cambridge; 2013.
16. Quay P, Sonnerup R, Westby T, Stutsman J, McNichol A. Changes in the C-13/C-12 of dissolved inorganic carbon in the ocean as a tracer of anthropogenic CO₂ uptake. *Global Biogeochemical Cycles*. 2003;17:1004.
17. Takahashi T, Sutherland SC, Wanninkhof R, Sweeney C, Feely RA, Chipman DW. Climatological mean and decadal changes in surface ocean pCO₂ and net sea-air CO₂ flux over the global oceans. *Deep Sea Res. II*. 2008;56:554-577.
18. Graven HD, N. Gruber N, Key S, Khatiwala S, Giraud X. Changing controls on oceanic radiocarbon: New insights on shallow-to-deep ocean exchange and anthropogenic CO₂ uptake. *J. Geophys. Res. Oceans*. 2012;117:C10005.
19. Gruber N, Gloor M, Mikaloff Fletcher SE, Doney SC, Dutkiewicz S, Follows ML, et al. Oceanic source, sinks and transport of atmospheric CO₂. *Global Biochem. Cycles*. 2009;23.
DOI: 10.1029/2008GB003349
20. Sabine CL, Feely RA, Gruber N, Key RM, Lee K, Bullister JL, et al. The oceanic sink for the anthropogenic CO₂. *Science*. 2004;305(5682):367-371.
21. Waugh DW, Hall TM, McNeil BI, Key R, Matear RJ. Anthropogenic CO₂ in the oceans estimated using transit time distributions. *Tellus B*. 2006;58:376-389.
22. Khatiwala S, Primeau F, Hall T. Reconstruction of the history of anthropogenic CO₂ concentrations in the ocean. *Nature*. 2009;462:346-349.
23. Sabine CL, Tanhua T. Estimation of anthropogenic CO₂ inventories in the ocean, *Annual Rev. Mar. Sci*. 2009;2:175-198.
DOI: 10.1146/annurev-marine-120308-080947
24. Manning AC, Keeling RF. Global oceanic and land biotic carbon sinks from the Scripps atmospheric oxygen flask sampling network. *Tellus*. 2006;58B:95-116.
25. Sarmiento JL, Gruber N. Sinks for anthropogenic carbon. *Phys. Today*. 2002; 55:30-36.
26. Schimel DS, House JI, Hibbard KA, Bousquet P, Ciais P, Peylin P. Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems. *Nature*. 2001;414:169-172.
27. Revelle R, Suess H. Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO₂ during past decades. *Tellus*. 1957;9:18-27.
28. Holmen K. The global carbon cycle in Earth system science: From biogeochemical cycles to global change. Jacobson MC, Charlson RJ, Rodhe H, Orians GH, editors. Academic Press, New York. 2000;282-321.
29. Stumm W, Morgan JJ. Aquatic chemistry. An introduction emphasizing chemical equilibria in natural waters. John Wiley & Sons, New York; 1970.
30. NOAA. Ocean temperature data base. Available:<ftp://ftp.ncdc.noaa.gov/pub/data/mlost/operational/products/>
(Accessed 5 March 2015)
31. Carbon dioxide concentration in the atmosphere from 1832 to 2013. Available:ftp://ftp.ncdc.noaa.gov/pub/data/paleo/icecore/antarctica/law/law_co2.txt
(Accessed 5 March 2015)
32. Thomson AM, Calvin KV, Smith SJ, Kyle GP, Volke A, Patel P, et al. RCP4.5: A Pathway for stabilization of radiative forcing by 2100. Joint Global Change Research Institute, Pacific Northwest National Laboratory and the University of Maryland, 5825 University Research Court, College Park, MD 20740; 25.
33. Farquhar GD, Roderick ML. Pinatubo, diffuse light and the carbon cycle. *Science*. 2003;299:1997-1998.

34. Sage R, Kubien DS. Temperature response of C3 and C4 photosynthesis. *Plant, Cell and Environment*. 2007; 30:1086-1106.
35. Monson KR, Stidham MA, Williams III GJ, Edwards GE, Uribe GE. Temperature dependence of photosynthesis in *Agropyron smithii* rydb. *Plant Physiol*. 1982;69:921-928.
36. Böhm F, Haase-Schramm A, Eisenhauer A, Dullo W-C, Joachimski MM, Lehnert H, Reitner J. Evidence for preindustrial variations in the marine surface water carbonate system from coralline sponges. *Geochemistry, Geophysics, Geosystem*. 2002;3(3).
DOI: 10.1029/2001GC000264
37. Scripps. Graphs Gallery. Global Stations Isotopic ¹³C Trends.
Available:http://scrippsco2.ucsd.edu/graphics_gallery/isotopic_data/global_stations_isotopic_13c_trends
(Accessed 20 Feb 2016)
38. Ioue HJK, Sugimura Y, Fushimi K. pCO₂ and ¹³δC in the air and surface sea water in the western North Pacific. *Tellus*. 1987;39B:228-242.

© 2016 Ollila; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
<http://sciencedomain.org/review-history/15789>