QUANTIFYING THE UPTAKE OF FOSSIL FUEL CARBON DIOXIDE BY THE OCEANS

40 Years of Research 1964-2004

In 1957 Dave (Charles David) Keeling from Scripps Institute of Oceanography started the now world-famous time series of atmospheric CO_2 measurements at Mauna Loa, Hawaii (Figure 1). After a few years a rise in CO_2 was apparent, at first controversial due to suggested measurement errors, but already in the early 1960's it was recognized the steady increase was real and attributable to the burning of fossil fuels.

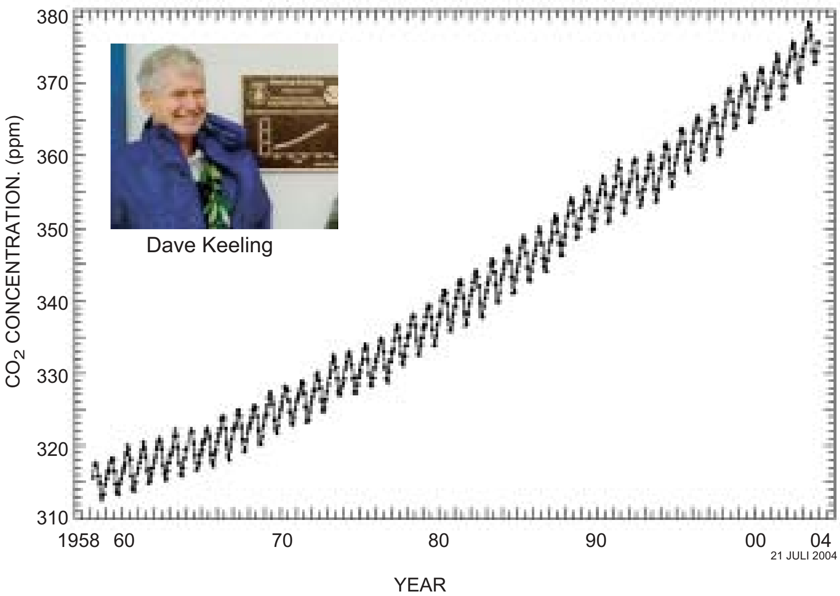


Fig. 1. Dave Keeling and his famous curve of increasing atmospheric carbon dioxide at Mauna Loa over the 1957-2004 period, to be continued. Taken from: http://cdiac.esd.ornl.gov/trends/co2/sio-mlo.htm

Henk Postma of the Netherlands Institute for Sea Research, while staying for a while at Scripps, in 1964 wrote an article in the two years young Netherlands Journal of Sea Research in which the fundamentals of the exchange of oxygen and carbon dioxide between ocean and atmosphere were established. This procedure was worked out for the case of the Pacific Ocean. While realizing the poor quality of some of the data he used, the procedure gave a tentative geographical pattern of exchange of carbon dioxide between the Pacific Ocean and the atmosphere (Figure 2). The shaded areas are the regions where carbon dioxide is outgassing from the ocean to the atmosphere. Immediately Henk Postma recognized that the pattern which existed before the addition of carbon dioxide from fossil fuels can in principle be determined by the same procedure. It was evident that the same procedure would show larger outgassing regions before fossil fuel burning started. In other words, owing to the combustion of fossil fuel, the escape areas have slightly decreased in size. In view of the limited accuracy of the data, Henk Postma did not further quantify this, but speculated that a future 25% increase of atmospheric CO_2 would already cause the high latitude outgassing belts to vanish completely, while the broad equatorial outgassing region would persist much longer. The increase of CO_2 in the oceans due to uptake of excess CO_2 from fossil fuel burning was, in principle, directly measurable (Postma,

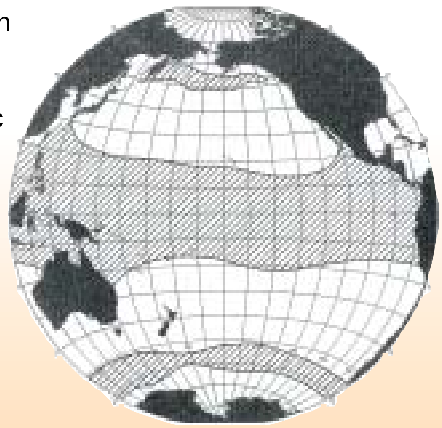


Fig. 2. Tentative geographical pattern of exchange of carbon dioxide between the Pacific Ocean and the atmosphere. Areas where carbon dioxide is transferred from the ocean to the atmosphere are shaded. Taken from Postma (1964).

Henk Postma in about early 1960's.

1964). The basic principles required for such an approach were also well understood at that time (e.g., correction of *in situ* Dissolved Inorganic Carbon (DIC) measurements for changes due to remineralization of soft tissue and dissolution of $CaCO_3$, comparison with “initial” or “preformed” concentrations at the sea surface).

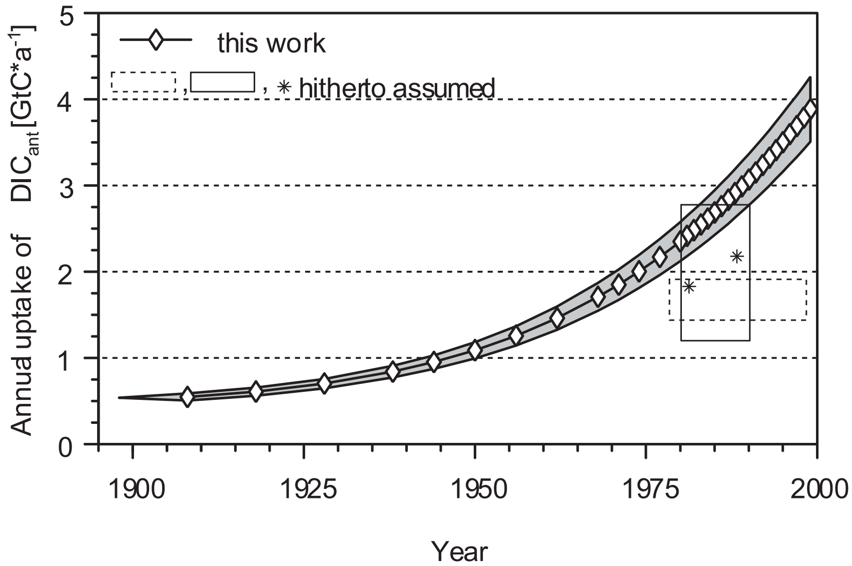
However, it was not until an extensive and reasonably high-quality data set for DIC and alkalinity was collected during the GEOSECS expeditions of the 1970's, that the full potential of such an approach was recognized and formalized. Brewer [1978] and Chen and Millero [1979] independently published formal approaches to extract the small excess (anthropogenic) component (order of 40 micromoles per kg seawater) from the large and strongly varying natural background DIC concentration (order 2000 micromol kg^{-1}). They demonstrated the approach using data collected during the GEOSECS Atlantic Survey. As Brewer [1978] noted, “the oceanic CO_2 concentration is indeed increasing with time….. this increase can be measured directly, and the record of this increase is written in the interleaved structure of oceanic water masses.”

Immediately the approach was criticized by sceptical scientists submitting comment articles to various journals. At that time (1978) the undersigned had just started the PhD research in the laboratory of Peter Brewer at Woods Hole, after having become enthusiastic for sea research during the Oceanography course of Henk Postma in 1974. The negative comments by others led to much discussion in our laboratory, and rapid writing of rebuttal statements by Peter Brewer. Eventually due to these criticisms the method fell out of use, except for Arthur Chen who continued to use it in various ocean regions, culminating in a review [Chen, 1993] which included an estimate of the global ocean inventory of excess (i.e. due to fossil fuel) CO_2 for the year 1980.

If we were ever going to have an accurate estimate of excess CO_2 in the oceans, we first should make major improvements in the accuracy of DIC measurements. With painstaking efforts Andy Dickson of Scripps realized the production and distribution of certified standards of CO_2 in seawater, as well as detailed measurement protocols. At the time Andy was visiting us at NIOZ and after a more and more cheerful dinner was amazed by the novel VacuVin rubber cork we used to seal off the final bottle of wine. The next day I gave him one of these Dutch inventions, which he gratefully accepted but at same time said he did not need it, as standard bottles always have to be completely emptied right away. Ever since the early 1990's, his methods and standards have been applied rigorously on all our cruises, and as a result the accuracy of the DIC global dataset has improved greatly.

Mario Hoppema graduated in 1991 under supervision of Henk Postma and he is now working at the Alfred Wegener Institute for Polar and Marine Research in Bremerhaven. Mario realized that this accuracy would allow direct observation of the DIC increase. By comparing several repeat cruises in the Weddell Sea, we were the first ever to report direct observations of increasing DIC in the deep ocean [*Hoppema et al.*, 1998].

Fig. 3. Annual uptake of anthropogenic CO_2 by the world oceans. The shaded area depicts the range between the upper and lower bound due to over- and underestimation of the ocean ventilation rates, respectively. The uptake rates hitherto assumed by common wisdom are indicated by the solid box, by stars and by the dashed box for various work by others, see further Thomas et al., 2001.



Meanwhile the same accuracy was applied in the JGOFS/WOCE Global CO_2 ocean survey in the middle of the 1990's. Simultaneously there was a renaissance of the indirect approach by calculation procedures as pioneered by Postma, Brewer, Chen and Millero, but now more comfortably relying on high accuracy ocean data. Nicki Gruber introduced major refinements of the calculation procedure, and his so-called ΔC^* method was widely accepted as a solid method to calculate the ocean inventory of excess CO_2 from the global oceans dataset [Gruber et al., 1996]. Soon others developed significantly different approaches with the same goal of estimating the excess CO_2 in the oceans [e.g. Goyet et al., 1999].

Helmuth Thomas having previously worked at Kiel, Warnemuende and Hamburg, came to NIOZ in 1998 in the context of the Netherlands Bremen Oceanography program. While preparing for a major North Sea cruise program to validate the "continental shelf pump hypothesis" he also found the time to visit Australia to collaborate with Matthew England. Together they developed yet another approach to estimate the excess CO_2 in the oceans. The manuscript was heavily criticized by the reviewers because over the years 1980-1989 their annual ocean CO_2 uptake at 2.4-3.1 PgC per year was far too high compared to common 'wisdom' (Figure 3). However the paper was eventually published in 2001 [Thomas et al, 2001]. Some years later such higher ocean CO_2 uptake for the era 1980-1989 has appeared to be evident, and common wisdom has been corrected upwards (Sabine et al., 2004). Nowadays, combining the JGOFS/WOCE survey with the Gruber approach, it is shown that the oceans have taken up 48% of fossil fuel emission over the 1800-1990 era, and 32% over the 1980-1999 era (Table 1). Meanwhile the North Sea program of four cruises in four seasons in 2001-2002 was underway, and resulted in an article published in Science in May 2004 [Thomas et al., 2004]. We had proven that, yes indeed, continental shelf seas are a major sink of excess CO_2; when extrapolating to all coastal seas worldwide perhaps as much as 20% of the overall ocean uptake of fossil fuel CO_2 is via coastal seas. The inevitable comment by some others, and our response, were a *déja-vu* of the early days with Brewer in Woods Hole. Other colleagues however really appreciated the work. This led to an offer Helmuth Thomas could not refuse, and at new year 2005 it is quiet in the CO_2 laboratory at NIOZ, but we will start again, with new staff and new projects continuing the 40 years strong tradition.

Table 1. Anthropogenic CO2 budget for the anthropocene (1800 to 1994) and for the decades 1980-1999. See further Sabine et al (2004).

	CO2 Sources and Sinks [Pg C] = [Petagram C] = [1015 gram Carbon]	1800 to 1994 [Pg C]	1980 to 1999 [Pg C]
	Constrained sources and sinks		
(1)	Emissions from fossil fuel and cement production	244 + 20	117 + 5
(2)	Storage in the atmosphere	-165 + 4	-65 + 1
(3)	Uptake and storage in the oceans	-118 + 19	-37 + 8
	Inferred net terrestrial balance		
(4)	Net terrestrial balance = [-(1) - (2) - (3)]	39 + 28	-15 + 9

After all some lessons are obvious: never underestimate the pioneer Henk Postma; good concepts often exist already before the data are accurate enough to verify and develop them further; accurate data leads to refined concepts; science is more than Nature or Science, so keep an eye on Geophysical Research Letters; and whenever you publish something original, be prepared for some by-standers to submit comment papers as their cheap route to fame.

Acknowledgements.

The pioneering contribution of Henk Postma was mentioned to me by Doug Wallace, and this text is largely based on Postma (1964) and Wallace (2001), including verbatim citations. Henk Postma was much indebted to Dave Keeling for valuable comments, while Dave Keeling also plays a key role in the certified standards program of Andy Dickson. His son Ralph Keeling very well understood the same relationships of oxygen and carbondioxide as used by Henk Postma, and pioneered the very accurate detection of decreasing O_2 in the atmosphere due to fossil fuel burning as a sophisticated tool to constrain the fate of fossil fuel CO_2 in the oceans. Texel, 19 January 2005, Hein de Baar.

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