# Correct Timing is Everything - Also for CO2 in the Air

**Guest Editorial by Tom V. Segalstad**
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In a paper recently published in the international peer-reviewed journal *Energy & Fuels*, Dr. Robert H. Essenhigh (2009), Professor of Energy Conversion at The Ohio State University, addresses the residence time (RT) of anthropogenic $CO_2$ in the air. He finds that the RT for bulk atmospheric $CO_2$, the molecule $^{12}CO_2$, is ~5 years, in good agreement with other cited sources (Segalstad, 1998), while the RT for the trace molecule $^{14}CO_2$ is ~16 years. Both of these residence times are much shorter than what is claimed by the IPCC. The rising concentration of atmospheric $CO_2$ in the last century is not consistent with supply from anthropogenic sources. Such anthropogenic sources account for less than 5% of the present atmosphere, compared to the major input/output from natural sources (~95%). Hence, anthropogenic $CO_2$ is too small to be a significant or relevant factor in the global warming process, particularly when comparing with the far more potent greenhouse gas water vapor. The rising atmospheric $CO_2$ is the outcome of rising temperature rather than vice versa. Correspondingly, Dr. Essenhigh concludes that the politically driven target of capture and sequestration of carbon from combustion sources would be a major and pointless waste of physical and financial resources.

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Essenhigh (2009) points out that the IPCC (Intergovernmental Panel on Climate Change) in their first report (Houghton *et al.*, 1990) gives an atmospheric $CO_2$ residence time (lifetime) of 50-200 years [as a "rough estimate"]. This estimate is confusingly given as an adjustment time for a scenario with a given anthropogenic $CO_2$ input, and ignores natural (sea and vegetation) $CO_2$ flux rates. Such estimates are analytically invalid; and they are in conflict with the more correct explanation given elsewhere in the same IPCC report: *"This means that on average it takes only a few years before a $CO_2$ molecule in the atmosphere is taken up by plants or dissolved in the ocean"*.

Some 99% of the atmospheric $CO_2$ molecules are $^{12}CO_2$ molecules containing the stable isotope $^{12}C$ (Segalstad, 1982). To calculate the RT of the bulk atmospheric $CO_2$ molecule $^{12}CO_2$, Essenhigh (2009) uses the IPCC data of 1990 with a total mass of carbon of 750 gigatons in the atmospheric $CO_2$ and a natural input/output exchange rate of 150 gigatons of carbon per year (Houghton *et al.*, 1990). The characteristic decay time (denoted by the Greek letter tau) is simply the former value divided by the latter value: 750 / 150 = *5 years*. This is a similar value to the *~5 years* found from $^{13}C/^{12}C$ carbon isotope mass balance calculations of measured atmospheric $CO_2$ $^{13}C/^{12}C$ carbon isotope data by Segalstad (1992); the *~5 years* obtained from $CO_2$ solubility data by Murray (1992); and the *~5 years* derived from $CO_2$ chemical kinetic data by Stumm & Morgan (1970).

Revelle & Suess (1957) calculated from data for the trace atmospheric molecule $^{14}CO_2$, containing the radioactive isotope $^{14}C$, that the amount of atmospheric *"CO2 derived from industrial fuel combustion"* would be only 1.2% for an atmospheric $CO_2$ lifetime of 5 years, and 1.73% for a $CO_2$ lifetime of 7 years (Segalstad, 1998). Essenhigh (2009) reviews measurements of $^{14}C$ from 1963 up to 1995, and finds that the RT of atmospheric $^{14}CO_2$ is ~16 (16.3) years. He also uses the $^{14}C$ data to find that the time value (exchange time) for variation of the concentration difference between the northern and southern hemispheres is ~2 (2.2) years for atmospheric $^{14}CO_2$. This result compares well with the observed hemispheric transport of volcanic debris leading to "the year without a summer" in 1816 in the northern hemisphere after the 1815 Tambora volcano cataclysmic eruption in Indonesia in 1815.

Sundquist (1985) compiled a large number of measured RTs of $CO_2$ found by different methods. The list, containing RTs for both $^{12}CO_2$ and $^{14}CO_2$, was expanded by Segalstad (1998), showing a total range for all reported RTs from 1 to 15 years, with most RT values ranging from 5 to 15 years. Essenhigh (2009) emphasizes that this list of measured values of RT compares well with his calculated RT of 5 years (atmospheric bulk $^{12}CO_2$) and ~16 years (atmospheric trace $^{14}CO_2$). Furthermore he points out that the annual oscillations in the measured atmospheric $CO_2$ levels would be impossible without a short atmospheric residence time for the $CO_2$ molecules.

Essenhigh (2009) suggests that the difference in atmospheric $CO_2$ residence times between the gaseous molecules $^{12}CO_2$ and $^{14}CO_2$ may be due to differences in the kinetic absorption and/or dissolution rates of the two different gas molecules.

With such short residence times for atmospheric $CO_2$, Essenhigh (2009) correctly points out that it is impossible for the anthropogenic combustion supply of $CO_2$ to cause the given rise in atmospheric $CO_2$. Consequently, a rising atmospheric $CO_2$ concentration must be natural. This conclusion accords with measurements of $^{13}C/^{12}C$ carbon isotopes in atmospheric $CO_2$, which show a maximum of 4% anthropogenic $CO_2$ in the atmosphere (including any biogenic $CO_2$), with 96% of the atmospheric $CO_2$ being isotopically indistinguishable from "natural" inorganic $CO_2$ exchanged with and degassed from the ocean, and degassed from volcanoes and the Earth's interior (Segalstad, 1992).

Essenhigh (2009) discusses alternative ways of expressing residence time, like fill time, decay time, e-fold time, turnover time, lifetime, and so on, and whether the Earth system carbon cycle is in dynamic equilibrium or non-equilibrium status. He concludes (like Segalstad, 1998) that the residence time is a robust parameter independent of the status of equilibrium, and that alternative expressions of the residence time give corresponding values.

It is important to compare Essenhigh's (2009) results with a recently published paper in *PNAS* by Solomon *et al.* (2009), the first author of which (Susan Solomon) co-chairs the IPCC Working Group One, the part of the IPCC that deals with physical climate science. This paper was published after Essenhigh had submitted his manuscript to *Energy & Fuels*.

The message of Solomon *et al.* (2009) is that there is an irreversible climate change due to the assimilation of $CO_2$ in the atmosphere, solely due to anthropogenic $CO_2$ emissions. From quantified scenarios of anthropogenic increases in atmospheric $CO_2$, their implication is that the $CO_2$ level flattens out asymptotically towards infinity, giving a residence time of more than 1000 years (without offering a definition or discussion of residence time or isotopic differences): "a quasi-equilibrium amount of $CO_2$ is expected to be retained in the atmosphere by the end of the millennium that is surprisingly large: typically ~40% of the peak concentration enhancement over preindustrial values (~280 ppmv)". The authors' Fig. 1, i.a. shows a peak level at 1200 ppmv atmospheric $CO_2$ in the year 2100, levelling off to an almost steady level of ~800 ppmv in the year 3000. It is not known how their 40% estimate was derived.

Solomon *et al.* (2009) go on to say that "this can be easily understood on the basis of the observed instantaneous airborne fraction ($AF^{peak}$) of ~50% of anthropogenic carbon emissions retained during their build-up in the atmosphere, together with well-established ocean chemistry and physics that require ~20% of the emitted carbon to remain in the atmosphere on thousand-year timescales [quasi-equilibrium airborne fraction ($AF^{equil}$), determined largely by the Revelle factor governing the long-term partitioning of carbon between the ocean and atmosphere/biosphere system]".

Solomon *et al.* (2009) have obviously not seriously considered the paper by Segalstad (1998), who addresses the 50% "missing sink" error of the IPCC and shows that the Revelle evasion "buffer" factor is ideologically defined from an assumed model (atmospheric anthropogenic $CO_2$ increase) and an assumed pre-industrial value for the $CO_2$ level, in conflict with the chemical *Henry's Law* governing the fast ~1:50 equilibrium partitioning of $CO_2$ between gas (air) and fluid (ocean) at the Earth's average surface temperature. This $CO_2$ partitioning factor is strongly dependent on temperature because of the temperature-dependent retrograde aqueous solubility of $CO_2$, which facilitates fast degassing of dissolved $CO_2$ from a heated fluid phase (ocean), similar to what we experience from a heated carbonated drink.

Consequently, the IPCC's and Solomon *et al.*'s (2009) non-realistic carbon cycle modelling and misconception of the way the geochemistry of $CO_2$ works simply defy reality, and would make it

impossible for breweries to make the carbonated beer or soda "pop" that many of us enjoy (Segalstad, 1998).

So why is the correct estimate of the atmospheric residence time of $CO_2$ so important? The IPCC has constructed an artificial model where they claim that the natural $CO_2$ input/output is in static balance, and that all $CO_2$ additions from anthropogenic carbon combustion being added to the atmospheric pool will stay there almost indefinitely. This means that with an anthropogenic atmospheric $CO_2$ residence time of 50 - 200 years (Houghton, 1990) or near infinite (Solomon *et al.*, 2009), there is still a 50% error (nicknamed the "missing sink") in the IPCC's model, because the measured rise in the atmospheric $CO_2$ level is just half of that expected from the amount of anthropogenic $CO_2$ supplied to the atmosphere; and carbon isotope measurements invalidate the IPCC's model (Segalstad, 1992; Segalstad, 1998).

The correct evaluation of the $CO_2$ residence time -- giving values of about 5 years for the bulk of the atmospheric $CO_2$ molecules, as per Essenhigh's (2009) reasoning and numerous measurements with different methods -- tells us that the real world's $CO_2$ is part of a dynamic (i.e. non-static) system, where about one fifth of the atmospheric $CO_2$ pool is exchanged every year between different sources and sinks, due to relatively fast equilibria and temperature-dependent $CO_2$ partitioning governed by the chemical Henry's Law (Segalstad 1992; Segalstad, 1996; Segalstad, 1998).

Knowledge of the correct timing of the whereabouts of $CO_2$ in the air is *essential* to a correct understanding of the way nature works and the extent of anthropogenic modulation of, or impact upon, natural processes. Concerning the Earth's carbon cycle, the anthropogenic contribution and its influence are so small and negligible that our resources would be much better spent on other *real* challenges that are facing mankind.

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