

Carbon Isotope Mass Balance Modelling of Atmospheric vs. Oceanic CO₂

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Stable ¹³C/¹²C isotope ratios, expressed as δ¹³C vs. PDB, give us the only way to unequivocally determine the fraction of anthropogenic CO₂ in the atmosphere. The natural atmospheric CO₂ reservoir has δ¹³C ≈ -7‰ when in isotopic equilibrium with marine HCO₃⁻ and CaCO₃. CO₂ from burning of fossil-fuel and biogenic materials has δ¹³C ≈ -26‰.

A pre-industrial CO₂ value of 280 ppmv in air was assumed by IPCC based on selected low value CO₂ data from ice cores (omitting measured high values up to 7,400 ppmv), matched with contemporary measurements by transposition of data with different ages (Jaworowski et al. 1992). IPCC claims that the rise in CO₂ to 353 ppmv in 1990 and 379 ppm in 2005 is only due to anthropogenic CO₂ (IPCC 1990, 2007).

δ¹³C reported for atmospheric CO₂ was -7.489‰ in Dec. 1978, decreasing to -7.807‰ in Dec. 1988 (Keeling et al. 1989). If the decreasing δ¹³C was only caused by mixing natural CO₂ with CO₂ from burning of fossil fuels or plants (~79%/~21% CO₂ mix; lifetime 50-200 years; IPCC 1989), the current atmospheric CO₂ δ¹³C should be -11, much lower than reported.

The December 1988 atmospheric CO₂ composition was computed for its 748 GT C (GT = 10¹⁵ g) total mass and δ¹³C = -7.807‰ for 3 components: (1) natural fraction remaining from the pre-industrial atmosphere; (2) cumulative fraction remaining from all annual fossil-fuel CO₂ emissions; (3) carbon isotope mass-balanced natural fraction. The masses of component (1) and (2) were computed for different atmospheric lifetimes of CO₂.

The result fits a lifetime of ~5 years, in agreement with ¹⁴C studies. The mass of all past fossil-fuel and biogenic emissions remaining in the current atmosphere was ~30 GT C or less, i.e. maximum ~4%, corresponding to an atmospheric concentration of ~14 ppmv. The implication of the ~5 year lifetime is that ~135 GT C (~18%) of the atmospheric CO₂ is dynamically exchanged each year.

Partitioning of CO₂ between atmosphere and hydrosphere is governed by Henry's Law, implying that 50-60 times more CO₂ is dissolved in the oceans than in the atmosphere. Due to the retrograde solubility of CO₂ in water, less CO₂ will be dissolved in water at higher temperatures.

At least 96% of the current atmospheric CO₂ comes from non-fossil-fuel sources, i.e. natural marine and juvenile sources. Hence for the atmospheric CO₂ budget marine degassing and juvenile degassing from e.g. volcanic sources must be much more important, and burning of fossil-fuel and biogenic materials much less important, than hitherto assumed.

Thermochemical modelling of calcium carbonate in seawater shows that pH would have to be decreased by 2 units, and H⁺ activity increased by 100, for Ca carbonate to dissolve at 25°C. By increasing atmospheric CO₂ this would by itself require 100 times the present CO₂ level. However, mineral buffers in the sea constitute an infinite buffer capacity (Stumm & Morgan 1970), making carbonate destructive ocean acidification from anthropogenic CO₂ impossible.

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