

Scientists diverge significantly when defining “concentrations” of gases like CO₂ in terms of their atmospheric fractions, and the definition of the term “mixing ratio” varies in more than one regard. Kariyathan et al. (2024) present a representative example where the different definitions are mixed and matched indiscriminately, casting doubt on the results that they present.

The study derives its results using the atmospheric transport model TM3 (Heimann and Körner, 2003), whose authors describe the determinant of tracer transport in terms of “kg tracer mass per kg air mass”; analysis of the units in their Equation (1) makes clear that the air mass must include water vapour. This definition of gas concentration, more simply termed the “mass fraction”, is indeed the scalar whose gradients determine diffusive transport (Kowalski et al., 2021). Unfortunately, however, Heimann and Körner (2003) termed this measure the “mixing ratio”, which conflicts with both of the popular (yet incompatible) definitions for that term, each referencing *dry* air. And the inclusion or exclusion of water vapour from the definition of this gas concentration is just one of two axes upon which disagreement revolves regarding the meaning of “mixing ratio”.

The other axis has to do with whether the fraction is defined on a molar or mass basis. Due to variations in the molecular masses of both air and its components, this distinction is not trivial; for example, although oxygen (O₂) is neither extremely heavy nor light, its atmospheric fraction of 20.95% in molar terms (Wallace and Hobbs, 2006) is quite different than in mass terms of 23.15% (Rogers and Yau, 1989). These two measures are affected differently when varying humidity modifies air’s effective molecular mass, which is one of many reasons why it is common to eliminate water vapour from the definition of the mixing ratio. But scientists from different disciplines do this in different ways: for meteorologists and other physicists, the mixing ratio is defined as the *mass* of the scalar per unit *mass* of dry air (e.g., Wallace and Hobbs, 2006); by contrast, atmospheric chemists prefer to define the mixing ratio as a *molar* fraction (e.g., Seinfeld and Pandis, 1998), also referencing dry air.

Kariyathan et al. (2024) are at variance with the transport model that they apply regarding both of the two axes described above. Whereas the Heimann and Körner (2003) transport model requires a mass-based fraction that references moist air (including water vapour), the methodology described indicates the use of a molar fraction that references dry air (excluding water vapour).

The methodology refers to the Jena Carboscope Atmospheric CO₂ Inversion, citing Rödenbeck et al. (2003), who define CO₂ "concentration" (the term "mixing ratio" is not used) in ppm – units that indicate a molar fraction. This Carboscope inversion leans upon the work of Conway et al. (1994) for their CO₂ flux database, which defines mixing ratios in ppm (in their Fig. 3), and refers to Komhyr et al. (1983) for CO₂ analyses. The latter publication describes a gas flow system that includes a trap to eliminate water vapour prior to analysis of dry air to determine CO₂ "concentrations" (in units of ppm; again, the term "mixing ratio" is not used).

All of this history points to a general lack of precision and consistency in defining the CO₂ "concentration" whose gradients determine diffusive transport. Kowalski et al. (2021) have shown that differences arising from distinct definitions of CO₂ "concentration" – as a mass fraction, molar fraction, or dry mass fraction – cause differences in derived diffusive transport magnitudes that are anything but trivial. And assuming that the requisite atmospheric state data are available, it is a simple accounting exercise to convert the CO₂ database to a mass fraction referencing moist air, and thereby feed the TM3 model with the data that it demands.

It would seem worthwhile for Kariyathan and colleagues to indulge in such an exercise, and determine whether their results are sensitive to the precise definition of "mixing ratio", as seems quite likely.

References

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