Review of Kowalski et al., Water vapor dynamics…

This Viewpoint paper offers a provocative perspective of the role of water vapor in atmospheric and leaf-scale gas exchange. It argues that water vapor dynamics (WVD) can be a driver of gas transport phenomena, using first-principles reasoning and thought experiments. The paper challenges the conventional (and useful) practice that expresses gas concentrations relative to dry air, especially under very humid conditions. It raises valid conceptual challenges to current modeling frameworks in both atmospheric chemistry and plant ecophysiology.

We thank Dr. Yakir for this considered assessment. Clearly the conventional practice of expressing gas fractions relative to dry air is often useful (lines 24-25 of our manuscript explicitly recognize this), and the stomatal conductance modelling framework successfully describes the coupled exchanges of water vapor and carbon dioxide within a broad range of environmental conditions. However, while this encompasses most growth conditions for terrestrial plants, it includes neither vital gas exchanges at very high leaf temperatures nor the transport of oxygen (a type III gas) in general. The point of our manuscript is to extend descriptions of gas concentrations and transport mechanisms to situations that conventional practice does not correctly describe.

As Dr. Yakir recognizes, our manuscript is about gas physics. Although we claim that this has implications that extend to plant ecophysiology, we prefer not to expand the scope of the paper to make it predominantly about leaf functioning during heatwaves. We hope that the reviewer(s) and editor will take this into account when considering our replies below.

However, the discussion of using mole fraction and partial pressure of dry air is not new, and the cases raised here apply mostly to extreme and rare cases, and remain speculative due to limited direct empirical validation. Some of the claims may be too strong like the relevance WVD in driving bulk airflow in atmospheric boundary layer dynamics. Or the suggestion of widespread invalidation of top-down flux inversion models (without demonstrating practical model biases attributable to neglecting WVD).

We think our discussion is new, but are eager to learn about previous studies that discuss the consequences of Dalton's law of partial pressures in this context.

Our paper is based on physics, not speculation, and direct empirical validation is readily available in literature data when taking Dalton's law into account. As an explicit example, practitioners of the Bowen ratio method (Perez et al., 1999; Savage et al., 2009) have characterised representative vertical water vapour pressure gradients ($\frac{de}{dz}$) as -100 Pa m^{-1} over actively transpiring vegetation. This decrease far exceeds the vertical pressure decline from the hydrostatic equation ($\frac{dp}{dz} = -\rho g$), which is only about -10 Pa m^{-1}. When taking the derivative of Dalton's law—our Eq. (1)—with respect to height

$$\frac{dp}{dz} = \frac{dp_d}{dz} + \frac{de}{dz}$$

these empirical data indicate that the dry-air pressure must *increase* with height ($\frac{dp_d}{dz} > 0$), implying that the oxygen concentration increases with height and therefore that oxygen diffusion is downward due to water vapor dynamics (see example in Table 1).

z (m)	*p* (Pa)	*e* (Pa)	p_d (Pa)	p_{N2} (Pa)	p_{O2} (Pa)	p_{Ar} (Pa)	χ_{O2} (ppt)
0.8	100010	2100	97910	76468	20561	881	205.6
1.8	100000	2000	98000	76538	20580	882	205.8

Table 1. An example of the evolution with height (z) of atmospheric pressure (p), the partial pressures of water vapor (e), dry air (p_d), nitrogen (p_{N2}), oxygen (p_{O2}), and argon (p_{Ar}), and the molar fraction of oxygen (χ_{O2}) over short, transpiring vegetation. Dry air's partial pressure is derived from Dalton's law, and its composition supposes every 1000 molecules to include 781 molecules of nitrogen, 210 of oxygen, and 9 of argon.

Since transpiration reduces near-surface oxygen by 200 ppm (0.2 ppt; Table 1) versus aloft, diffusion of oxygen (a Type III gas) is downward regardless of photosynthetic production. Yet we know that *net* oxygen transport over a photosynthetic surface is upward, making it clear that the vertical flux of oxygen from the hypoxic, near-surface layer towards higher, more aerobic regions of the boundary layer is non-diffusive in nature and depends on bulk airflow driven by water vapor dynamics.

Finally, our manuscript suggests that what is invalidated by neglect of water vapour dynamics is not necessarily top-down flux inversion models, but only their underlying assumptions. It is not inconceivable that such models could correctly describe sources and sinks despite mischaracterising the physical mechanisms of transport (e.g., see Yan et al., 2023 and especially the on-line discussion phase of that paper). However, this is unlikely to be true in tropical conditions where water vapor surpasses trace status.

References:

Perez, P. J., et al., 1999, Assessment of reliability of Bowen ratio method for partitioning fluxes, *Agricultural and Forest Meteorology*, **97**, 141–150.

Savage, M.J., et al., 2009, Bowen ratio evaporation measurement in a remote montane grassland: Data integrity and fluxes, *Journal of Hydrology*, **376**, 249–260, https://doi.org/10.1016/j.jhydrol.2009.07.038

Yan, Y. et al., 2023, A modeling approach to investigate drivers, variability and uncertainties in O_2 fluxes and O_2 : CO_2 exchange ratios in a temperate forest, *Biogeosciences*, **20**, 4087–4107, https://doi.org/10.5194/bg-20-4087-2023

The authors use sound theoretical reasoning to develop the WVD idea but extending these principles into stomatal decoupling, and macro-scale transport, relies on indirect support, and many of the supporting studies (e.g., Kowalski 2017; Kowalski et al., 2021, 2025) are from the same authors.

We agree with the referee's comment. The support, apart from the sound physics, is indeed indirect, but this does not imply it is incorrect. The hypoxic nature of very humid air is a direct consequence of Dalton's law of partial pressures when applied in an approximately isobaric context, as in the table/model above and also our Figure 1. Oxygen is consistently transported up its gradient from relatively hypoxic regions—where it is produced yet diluted by water vapor dynamics—toward drier, more aerobic regions. Such transport is independent of scale:

- From substomatal cavities to the exterior leaf environment (Kowalski, 2025);
- from near-surface air to higher regions of the boundary layer (Table 1, above); and
- from tropical rainforests to other areas of the world (Figure 1 of our manuscript).

In each case, net oxygen transport is oriented not by diffusion but rather bulk airflow. This makes clear that water vapor dynamics actuates both types of transport mechanisms.

Similarly, the idea that WVD, under high humidity and temperature, could lead to a physical decoupling of CO_2 uptake and H_2O loss in leaf gas exchange is intriguing. But validation with field or chamber measurements is badly missing.

Here we respectfully disagree with the referee. Numerous field and chamber measurements (Aparecido et al., 2020; de Kauwe et al., 2019; Diao et al., 2024; Krich et al., 2022; Marchin et al., 2023) have observed decoupling under heatwave conditions. Further validation is available via our re-analysis of the results of Scafaro et al. (2023) dataset. We confirmed via extensive personal communication with the authors (both Drs. Farquhar and Scafaro) that their model imposed constant values of p_{CO_2} and p_{O_2}even at leaf temperatures far exceeding 40ºC, thus short-circuiting dilution by water vapor. We multiplied these partial pressures by $\left(1 - \chi_{H_2O}\right)$ within the Scafaro et al. (2023) dataset—effectively correcting for the effects of dilution— and this improved the fit to observations of an assimilation temperature response function, and also reduced bias in Rubisco carboxylation limited assimilation rates (Fig. 1). Please, note that Scafaro´s dataset, as well as most existing studies, rarely contain field and chamber measurements exceeding 40ºC when the effects of decoupling are relevant, and the model bias remarkable (See Fig. 1).

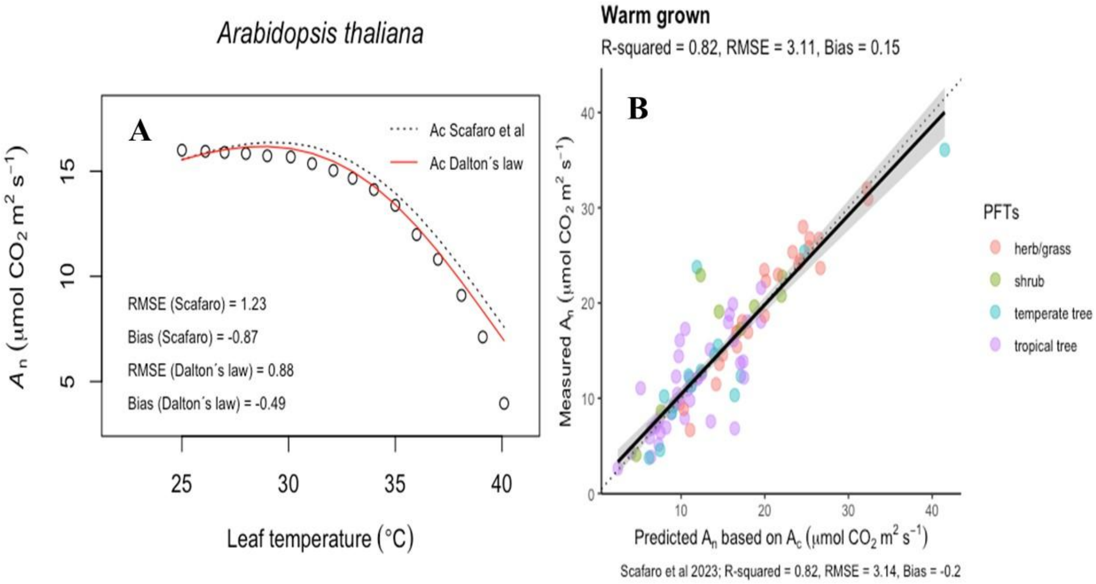

Figure 1. Observations, modelled simulations, and the predictability of the leaf temperature response of net CO_2 assimilation (A_n). A The A_n temperature response of *Arabidopsis Thaliana*. As in Scafaro et al.[1], points are observations and the curves are the modelled Rubisco carboxylation limited assimilation rates (A_c) with Rubisco deactivation included. Model partial pressures are estimated via the dry-air molar fraction (c, dashed line) or moist-air molar fraction (χ; solid red line). **B** Predictions of A_c which included Rubisco deactivation but with partial pressures estimated via the moist-air molar fraction (χ; dashed line).

We prefer not to include the results shown in Figure 1 above in this paper that focuses on atmospheric composition and transport mechanisms. Should we succeed in publishing this paper regarding the physics, we will then aspire to publish a follow-up manuscript that specifically regards leaf functioning, and will include field or chamber measurements. However, if the referees and editor feel that their inclusion is necessary, then we will be willing to oblige.

In fact, the widely used model of Farquhar et al 1980 deals with some of the aspects of CO2 dilution by water vapor in the substomatal space, but is not cited or discussed. in fact, all leaf gas exchange measurements are also corrected for humidity dilution in calculating net assimilation.

Farquhar et al (1980) make no mention, neither of water vapor, humidity, nor dilution. We think the paper Dr. Yakir has in mind is that of von Caemmerer and Farquhar (1981), which we did cite and which indeed does account for dilution of carbon dioxide by water vapor.

However, there are two aspects of this paper that are criticizable and upon which we think our own manuscript improves:

1. Because dilution by water vapor is hidden in an appendix of their paper, it has not generally been recognized by ecophysiologists. This likely explains why high-temperature suppression of photosynthesis has been attributed solely to biochemical processes (as we note at line 171) and may even explain why dilution was excluded from the model of Scafaro et al. (2023), even with Dr. Farquhar as a co-author. Hence our critical remark at line 165 (such approaches "obscure two key consequences of water vapor dynamics when humidity achieves bulk status"); and
2. The description of diffusion based on gradients in the mole fraction (Jarman, 1974; von Caemmerer and Farquhar, 1981) represents a violation of Newton's laws. This is demonstrated both in a previous publication (Kowalski et al., 2021) and in two open discussions that can be accessed here:
    a. https://doi.org/10.5194/egusphere-2025-2814
    b. https://doi.org/10.5194/egusphere-2025-2705-RC1

    Rather, because of the key role played by mass/inertia in defining motion, it is the mass fraction whose gradients determine diffusion and which must be used to distinguish diffusive from non-diffusive transport (Kowalski, 2017; see also the Appendix of our manuscript). The von Caemmerer and Farquhar (1981) paper does not recognize non-diffusive transport by bulk airflow exiting stomata. While this mischaracterizes the physics of leaf gas exchanges with the atmosphere, in most studies its effect would be negligible. However, when studying impacts of very high temperature on gas transport, ignoring or misrepresenting water vapor dynamics does matter.

Reference:

Farquhar, G.D., von Caemmerer, S. and Berry, J. A., 1980, A biochemical model of photosynthetic CO_2 assimilation in leaves of C3 species, *Planta*, **149**, 78–90.

In discussing the links to biochemical rates, specifically in photosynthesis, some reference should be made to the fact that dissolved CO2 is the end member via Henry's law and other local factors at the site.

We agree. Therefore, we propose to change the sentence that begins at line 145 from

- "This assumes proportional CO_2 and water vapour flux/gradient ratios based on Graham's law (Jones, 2014) and allows estimating the dry-air molar CO_2 fraction (c_i) of substomatal cavities, presumed a suitable proxy for the p_i of CO_2 (Gaastra, 1959), which is a key photosynthetic determinant", to
- "This assumes proportional CO_2 and water vapour flux/gradient ratios based on Graham's law (Jones, 2014) and allows estimating the dry-air molar CO_2 fraction

(c_i) of substomatal cavities, presumed a suitable proxy for the p_i of CO_2 (Gaastra, 1959), which determines CO_2 dissolution via Henry's law and thereby photosynthesis".

Rhetoric like "air is water vapor; water vapor is air" is somewhat distracting

We see the referee's point, but still believe this rhetoric is important to get the reader's attention. Grasping these ideas is essential to understanding the influence of water vapor dynamics on bulk airflow. Staying with the order of scales that is presented above, we note that:

- By pumping air into substomatal cavities, water vapor dynamics force bulk airflow out of stomata that enables up-gradient oxygen transport and, at very high temperatures, becomes relevant to the transport of both water vapor and carbon dioxide;
- By pumping air out of the surface, water vapor dynamics push the entire boundary layer upward and enables upward (up-gradient) transport of oxygen; and
- By pumping massive amounts of air into tropical rainforests, water vapor dynamics push air away from them and allows them to export oxygen to more aerobic regions.

The schematic showing decoupled CO_2 and H_2O fluxes is conceptually useful but would benefit from real data overlay (e.g., from gas exchange measurements during heatwaves) to illustrate feasibility.

Thank you for this comment, but observations of decoupled carbon dioxide and water vapor exchanges during heatwaves have been broadly observed by plant ecophysiologists (Aparecido et al., 2020; de Kauwe et al., 2019; Diao et al., 2024; Krich et al., 2022; Marchin et al., 2023). Here, we prefer to focus on the roles of atmospheric composition and transport mechanisms, not on the ecophysiology. While referring to these consequences for ecophysiology during heatwaves as observed in many recent studies, we therefore prefer not to include this in this manuscript.

Equations A5, and 2, could benefit from some relevant quantitative examples.

We thank the referee for this suggestion and intend to add statements leading the readers to the quantitative examples in the manuscript. Thus, we propose to add

- after Equation 2 that a quantitative example of this is depicted in Figure 1; and
- a final sentence to the Appendix stating that the consequences of Equation A5 are visualized in Figure 4.

Overall, the manuscript presents a thought-provoking argument that challenges long-standing assumptions in atmospheric and plant sciences. It presents a sound physical and conceptual relevance of water vapor as an important player in gas transport and exchange. It would benefit from: Stronger empirical support through simulations or re-analysis of published data. Moderation of rhetoric in places where established practices are critiqued.

We sincerely thank the referee for the time and work invested in our study. We hope that the discussion above convinces the referee that there is ample empirical support in the published literature. If we were to include empirical data in this manuscript, the focus would shift from the underlying physics to the ecophysiological consequences, which we really want to avoid in this manuscript.

Any specific suggestions for moderation of rhetoric would be most welcome.

I think the manuscript should be accepted for publication after moderate revision, particularly with a better balance of conceptual divergence with empirical grounding.

Again, we thank Dr. Yakir for his careful examination of our paper.