Please note that this “author’s response” is simply a copy/paste of my replies to the reviewers in the on-line discussion. The changes made as a consequence are those proposed in my replies to Reviewer 1.

**Reviewer 1**

I thank the anonymous referee for this constructive assessment of the manuscript, since several of the comments have enabled me to propose revisions that should improve clarity. The comments are repeated below in italicized font, followed by my replies in normal font.

*This manuscript presents a theoretical, physically based model to explain the possible occurrence of nondiffusive exchange of gases between plant leaves and the atmosphere. The approach is founded in fluid dynamics and makes some simple assumptions in arguing that plant physiologists have been incorrect in their treatment of gas exchange processes. The article is really more like an opinion piece in the way it's written, starting from the first sentence of the introduction. If the author wants to develop a dialog, a more moderate tone might help.*

For decades now, reviewers have admonished me regarding the "tone" of my writing. Clearly it is a defect, and one that I have worked to improve, but apparently without great success. I am very much open to any specific suggestions that would improve the tone without changing the scientific meaning.

*The paper could be improved by starting with a clear statement of the evidence that there is a potential mistake in the conceptual framework underpinning leaf gas exchange, specifically the assumption that stomatal fluxes are always diffusive. The broad context of the "decoupling" of photosynthesis and transpiration is a widely observed phenomenon especially in response to heat waves. The author has developed a possible physical explanation for this observation. The paper could also be improved by clarifying a number of issues as described below.*

The introduction section, a lone paragraph of just four sentences, is intented as "a clear statement of the evidence that there is a potential mistake in the conceptual framework underpinning leaf gas exchange, specifically the assumption that stomatal fluxes are always diffusive." I have no doubt that other authors could state it more clearly, but have done my best in this regard.

*Specific comments*

*L9. "preserving cavity pressurization that is negligible as regards air composition." This part of the sentence could be a separate sentence because the total cavity pressure is an important and separate consideration from the partial pressures. Indeed, cavity pressurization caused by transpiration appears to be the main mechanism for oxygen emissions, according to the theory.*

Total cavity pressure is not separate consideration from the partial pressures, but rather directly linked via Dalton's law. This is the very basis of my analysis as reflected by the fact that it is mentioned in the first sentence of the manuscript.

*L10. Change "suppression" to "dilution"*

There are two processes that lead to depression of oxygen. Dilution is certainly one, but the other is displacement. Perhaps an examination of a stomatal cavity in light of the Ideal Gas Law will clarify this.

Consider a cavity of constant volume, and for simplicity at constant temperature, with an initial pressure (p1) and containing n1 moles of air. If transpiration adds a single water vapour molecule to the cavity, then some other molecule (very probably nitrogen) must exit, since n2>n1 implies pressurization (p2>p1) via the Ideal Gas Law, driving outward flow until pressurization is exhausted. Ultimately, the cavity is both enriched in water vapour and depleted in nitrogen, which will then tend to diffuse back inward while water vapour diffuses outward.

Now if we repeat this experiment five times, statistically we can expect expulsion of four nitrogen and one oxygen molecules. Oxygen is both diluted and displaced by transpiration. Note that in steady-state conditions, nitrogen is displaced outward but diffuses inward, and the two transport mechanisms cancel out such that there is no net transport of nitrogen (except, perhaps, for legumes or other nitrogen-fixing plants; I am no expert on nitrogen uptake). The same argument could be made regarding oxygen, but then we must take into account photosynthetic enrichment.

If we repeat the experiment a million times, then things get interesting for the vital gases. Of the million displaced molecules:

- about 780,000 will be nitrogen;

- nearly 210,000 will be oxygen, far exceeding what photosynthesis can add;

- thousands will be water vapour, whose departures represent non-diffusive vapor transport because they were pushed out;

- hundreds will be carbon dioxide, whose depletion (and subsequent diffusion) are not due to photosynthesis.

To me, it is clear that dilution is not the only process that reduces substomatal oxygen. Displacement also does so, implying non-diffusive transport. This is the point of the manuscript, and therefore I prefer not to change "suppression" to "dilution".

*L 59, It is confusing to say that cavity pressurization can be neglected, because in the abstract it is implied that cavity pressurization is not negligible.*

Context is very important. Clearly the same phenomenon can be negligible in one regard but not in another. For example, at 2 ppm methane plays a negligible role in determining the specific heat of air, but not in absorbing infrared ratiation.

The abstract says that cavity pressurization is "negligible **as regards air composition**" (line 11), but "not negligible **in the context of driving viscous flow**" (line 18; bold emphasis added in each case). To reduce confusion, I propose to modify the sentence mentioned at L 59 begins to specifically state that the context in which pressurization can be neglected is that of air composition, because it is about to be used in Eq. (7) to model the partial pressure of oxygen.

*L 90, here we see that pressurization is negligible but non nonzero…*

This is because the context of Table 1 is that of air composition, not dynamics. Again, to make this more clear, I propose to change the Table caption so that it begins with "Consequences of negligible stomatal-cavity pressurization regarding air composition."

*L 108110, I am not convinced that the substomatal cavity is dilute in oxygen. Inward diffusion will offset the vapor effects. It would be nice to see some evidence for this theory, such as in the isotopic composition of oxygen or carbon dioxide that might be altered in the process of biosphereatmosphere exchange.*

Substomatal cavities are dilute in oxygen because leaf gas emissions are dilute in oxygen. As I have written elsewhere in Copernicus open discussions (https://doi.org/10.5194/bg-2023-30-CC1), even with a modest evaporation rate and robust photosynthesis, less than 2% of the molecules emitted within substomatal cavities are oxygen (versus 21% in the atmosphere). (More than 98% are water vapour.) Thus, the combination of transpiration and photosynthesis results in dilution of stomatal cavities, driving inward oxygen diffusion.

Evidence of this in the isotopic composition of oxygen has long existed and is known as the "Dole effect", with tropospheric air richer in heavy oxygen than seawater (Dole, 1935). The massive inward diffusion of oxygen results in fractionation, with only the lightest oxygen molecules able to diffuse upstream against the jet and so be consumed by respiration within the stomatal cavity, leaving the atmopshere enriched in heavy oxygen. I did not include this in the paper because it seems likely to cause even more controversy.

Dole, M., 1935, The relative atomic weight of oxygen in water and in air, J. Chem. Phys., 4(4), 268-275.

*L 134135, It is hard to understand this sentence "If these increases in water vapour transport rates seem modest, versus what can be achieved by diffusion alone, they grow in importance when considered in combination with jet suppression 135 of photosynthesis."? Until one reads L 137139. This is another example of how the paper could be improved by putting the problem statement before the solution, instead of viceversa.*

I generally appreciate suggestions to improve the structure of my writing, but in this case cannot understand the referee's meaning.

This section of the paper addresses the influence of jets on transport of carbon dioxide and water vapour. It has three paragraphs whose themes appear in the first sentence of each: the first (L 116) addresses carbon dioxide, the second water vapour (L 129), and the third their relative behaviour (L 137) including water-use efficiency and decoupling. The sentence cited by the referee, as the last in the paragraph about water vapour, is intended guide the flow of the text to the following paragraph.

Perhaps if the referee could clarify what is meant by "problem statement" and "solution", I could understand how to improve this section of the paper.

*L 144145, It seems unnecessary to "cast doubt on the very meaning of stomatal conductance." Certainly the concept is useful, as is the concept of hydraulic conductance as it pertains to water flow through porous media, where both diffusion and mass flow occur.*

I disagree. Stomatal conductance describes diffusive fluxes as a function of concentration gradients, while hydraulic conductance describes non-diffusive fluxes as a function of pressurization. Physically, they are very dissimilar.

Physiologists often interpret stomatal conductance as meaning the degree to which stomata are open (e.g., Urban et al., 2017). Strictly speaking, however, it is a ratio of flux to concentration difference. In the diffusion-only paradigm, stomatal conductance for water vapour and carbon dioxide are coupled (via Graham's law), and covary with the degree of stomatal aperture. But non-diffusive transport, when not negligible, makes this not so. Within a stomatal aperture of fixed dimensions, a temperature increase to extreme values invalidates the paradigm, enhancing water vapour egress but inhibiting carbon dioxide ingress. This is best illustrated by the case of boiling (where the vapour pressure equals the total pressure, yielding a specific humidity of 100%). Gas exchange through the spout of a boiling tea kettle has nothing to do with diffusion:

- water vapour is the only gas present, and so cannot diffuse with no concentration gradient but has a large flux (infinite stomatal conductance) that is non-diffusive in nature (i.e., a jet);

- carbon dioxide cannot enter the kettle despite an enormous concentration gradient (zero stomatal conductance) because the jet is so strong that it cannot diffuse upstream.

(Recall that boiling can be achieved, either by raising the temperature at constant pressure, or by lowering the pressure at constant temperature.)

When state conditions tend towards boiling, stomatal conductance for water vapour increases but this does not mean that the aperture has expanded, and stomatal conductance for carbon dioxide decreases but this does not imply that the aperture has contracted. I believe, therefore, that jet transport casts doubt on the meaning of stomatal conductance.

Urban, J., et al., 2017, Increase in leaf temperature opens stomata and decouples net photosynthesis from stomatal conductance in pinus taeda and populus deltoides nigra, J. Exp. Bot., 68, 1757-1767.

**Citation**: https://doi.org/10.5194/egusphere-2024-1966-AC1

**Reviewer 2**

I thank the anonymous referee for the engaging discussion. Although pushing back against suggested changes, I appreciate this on-line forum as a space in which to rationalize decisions regarding wording and composition, and remain open to further suggestions to improve the manuscript. The referee's comments (italic font) are followed by my replies (normal font).

*I agree that the model of stomatal flux as exclusively diffusive is oversimplified; at times I've said that one person's diffusion is another's advection, and applying advective flux principles to stomata is likely to lead to new insights.*

I appreciate the reviewer's perceptive perspective.

*The parentheses aren't needed in equations 1-3, and 'mere trace' should perhaps be quantified more explicitly, perhaps as greater than 0.9% (argon) or 0.4% (water, on average), because many peoples' research careers depend on these key trace gases including CO2!*

Mathematically, the parentheses do not change these equations, and so they are not needed. However, they are included to focus attention on the partial pressure of dry air (line 30). I find them helpful as a reminder that, with negligible cavity pressurisation, humidification suppresses the partial pressure of dry-air and thereby its every component.

I worry that an attempt to quantify "mere trace" would open a can of worms. The most abundant trace gas is $CO_2$ at about 0.042% of the atmosphere. Its neglect would mean describing atmospheric composition with 99.958% accuracy, which seems acceptable. But where should we delineate the acceptable degree of accuracy? Can we confidently say that 99% is acceptable, but 97% is not? I have searched the literature, of not only atmospheric gases but science in general, for some definitive and citable statement regarding what is and is not negligible. I have found nothing concrete, and so hesitate to explicitly quantify "mere trace".

This sentence begins with the words "Dalton's law of partial pressures", which establish its context. As I have argued to the other reviewer, context is very important when determining what can and cannot be neglected. In the context of Dalton's law, $CO_2$ is negligible. Of course, it is not negligible in the context of atmospheric absorption of infrared radiation, but that is another story altogether.

*In equation 4, the delta implies a surplus or a deficit depending on direction (the text only states surplus)*

Line 36 defines Δ as denoting a surplus. Mathematically, a negative surplus is a deficit. Thus, $\Delta e>0$ describes a surplus of water vapour, whereas for dry-air component *i*, $\Delta p_i<0$ describes a deficit.

*54: This value still seems quite fast, even as an upper bound, but could be justified in more detail by explaining a bit more the contents of Kowalski 2017 as it applies to the present study*

An earlier draft of this manuscript included the following text:

> Newtonian physics identifies an air jet escaping stomata (Kowalski, 2017), here summarised. Air components have diverse momenta (kg m $s^{-1}$) including outward $H_2O$ and $O_2$, null $N_2$ and Ar, and inward $CO_2$. Air's momentum is the sum of its components' momenta. With $H_2O$ dominating stomatal gas exchange by orders of magnitude, air's momentum density equals the $H_2O$ flux density ($F_{H_2O}$; kg $m^{-2}$ $s^{-1}$) that quantifies transpiration. The outward airspeed is therefore the momentum-to-mass ratio $\frac{F_{H_2O}}{\rho}$

A colleague who helpfully read the manuscript suggested that, for a paper describing a model of oxygen's partial pressure inside stomata, this text is extraneous and distracting.

The purpose of this section of the paper is to establish that cavity pressurisation is negligible in the context of Dalton's law, **at most** $\Delta p$ = 0.0011 kPa. The reviewer says that "*This value still seems quite fast*", implying that I have likely overestimated *v* and therefore $\Delta p$. If anything, this buttresses the argument that pressurisation can be neglected ($\Delta p$ = 0). Therefore, I think my colleague was correct, and that there is no need to justify in more detail using *v* = 6 mm $s^{-1}$ as an upper bound.

*I'm having trouble fully following the paragraph on line 57. The difference is about 1 Pa, which isn't much. Is the argument that, even with extreme parameter values there is little reason to believe that delta_p is approximately zero such that positive delta_e implies negative delta_p of the other gases?*

I think the reviewer follows perfectly, but also that example values might illustrate this more clearly. Let's consider a "moderate VPD" (Aliniaeifard and van Meeteren, 2014), with $\Delta e$ = 1.17 kPa, and examine two cases when assessing dry air's partial pressure, between parentheses in Eq. (4):

1. If we use the upper bound of $\Delta p$ = 0.0011 kPa, then it must be depressed by 1.1689 kPa;
2. If we neglect pressurisation and use $\Delta p$ = 0, then it must be depressed by 1.17 kPa.

These outcomes are 99.9% the same, which I think justifies assuming $\Delta p$ = 0 in Eq. (4). I do not wish to add these example values to the manuscript, unless the reviewer and editor so prefer.

**Reference**

Sasan Aliniaeifard, Uulke van Meeteren, Natural variation in stomatal response to closing stimuli among *Arabidopsis thaliana* accessions after exposure to low VPD as a tool to recognize the mechanism of disturbed stomatal functioning, *Journal of Experimental Botany*, Volume 65, Issue 22, December 2014, Pages 6529–6542, https://doi.org/10.1093/jxb/eru370

*I still find the evidence to be by omission: if O2 can't leave stomatal cavities by diffusion, it must be 'jets'. But what do these jets look like, how do they 'burst' and do other mechanisms like Bernoulli pumping cause the transport in practice? To me the major weakness is a lack of description of how the jets work, for lack of a better word, in practice and if fluid mechanical simulations, conceptual models, or studies of 'bursting' when stomata open (or the 'thermostat' model that Joe Berry described) would be most fruitful for better understanding stomatal dynamics going forward.*

Rejecting long-embraced ideas can be a major challenge for advancing knowledge (Keynes, 1936), and I believe this applies to the assumption that diffusion alone transports gases through stomata. I would argue that, if $O_2$ cannot leave stomatal cavities by diffusion, then non-diffusive transport must be responsible. The terminology of "jets" may be appropriate as argued by Kowalski (2017), or it may not. Once it is accepted that non-diffusive transport exists, science can then address its mechanistic functioning as a next step. Does it occur as a steady stream, or in spurts? If the latter, are the spurts triggered by atmospheric turbulence (a Bernoulli effect), or by thermodynamic forcings, or what? Such questions certainly seem relevant to understanding stomatal control of gas exchanges, particularly at high temperatures. I share the referee's curiosity regarding these questions, but feel that they will be best addressed only once the scientific community accepts the relevance of non-diffusive transport.

**Reference**

Keynes, J. M., The General Theory of Employment, Interest and Money, Macmillan (1936)