

The boundary condition for the vertical velocity and its interdependence with surface gas exchange

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Abstract. The law of conservation of linear momentum is applied to surface gas exchanges, employing scale analysis to diagnose the vertical velocity (w) in the boundary layer. Net upward momentum in the surface layer is forced by evaporation (E) and defines non-zero vertical motion, with a magnitude defined by the ratio of E to the air density, as $w = \frac{E}{\rho}$. This is true even right down at the surface where the boundary condition is $w|_0 = \frac{E}{\rho|_0}$ (where $w|_0$ and $\rho|_0$ represent the vertical velocity and density of air at the surface). This Stefan flow velocity implies upward transport of a non-diffusive nature that is a general feature of the troposphere but is of particular importance at the surface, where it assists molecular diffusion with upward gas migration (of H₂O, e.g.) but opposes that of downward-diffusing species like CO₂ during daytime. The definition of flux-gradient relationships (eddy diffusivities) requires rectification to exclude non-diffusive transport, which does not depend on scalar gradients. At the microscopic scale, the role of non-diffusive transport in the process of evaporation from inside a narrow tube – with vapour transport into an overlying, horizontal air stream – was described long ago in classical mechanics, and is routinely accounted for by chemical engineers, but has been neglected by scientists studying stomatal conductance. Correctly accounting for non-diffusive transport through stomata, which can appreciably reduce net CO₂ transport and marginally boost that of water vapour, should improve characterizations of ecosystem and plant functioning.

1 Introduction

The vertical velocity (w) is a key variable in the atmospheric sciences, whose precise diagnosis is essential for numerous applications in meteorology. Above the boundary layer, the weather is largely determined by adiabatic adjustments to vertical motion that is slight compared to horizontal winds. Closer to the surface, even a tiny w can result in relevant transport; for example, in a typical boundary layer – with representative temperature ($T = 298\text{K}$), pressure ($p = 101325\text{ Pa}$), and CO₂ mass fraction (607 mg kg⁻¹; a molar ratio of about 400 ppm) – just 61 $\mu\text{m s}^{-1}$ of average vertical velocity is needed to waft a biologically significant 44 $\mu\text{gCO}_2\text{ m}^{-2}\text{ s}^{-1}$ (a CO₂ molar flux density of 1 $\mu\text{mol m}^{-2}\text{ s}^{-1}$). Modern anemometry cannot resolve such miniscule airflow (Lee, 1998), and generally w is immensurable at many scales so that it must be derived from other variables (Holton, 1992). Such diagnostic estimation is traditional in synoptic meteorology, but has been developed less rigorously near the surface boundary.

36

37 The characterization of boundary conditions for state and flow variables, in order to enable atmospheric
38 modelling at larger scales, is a fundamental goal of micrometeorology. Since w is an air velocity, its
39 boundary condition $w|_0$ describes the surface-normal or vertical motion of the gas molecules found
40 closest to the surface (at some height $z|_0$, very nearly but not exactly zero). The Navier-Stokes equations,
41 when applied to the lower atmosphere, are particularly sensitive to the conditions specified at the
42 boundary (Katul et al., 2004), and this lends great importance to $w|_0$ in the context of dynamic modelling.
43 Nevertheless, until now $w|_0$ has received inadequate attention in boundary-layer meteorology.

44

45 Micrometeorologists have made presuppositions regarding $w|_0$ without formal justification and in
46 contradiction to deductions from classical mechanics. The traditional hypothesis about near-surface winds
47 is that they flow parallel to underlying terrain (Kaimal and Finnigan, 1994; Wilczak et al., 2001) and
48 vanish at the surface (Arya, 1988), implying $w|_0 = 0$. This assumption underlies many derivations and
49 abets the prevailing belief that vertical exchanges are accomplished purely by molecular diffusion within
50 a millimeter of the surface (Foken, 2008), or purely by turbulent diffusion at heights of meters or more
51 within the atmospheric boundary layer. However, such a premise is inconsistent with the fact of net
52 surface gas exchange (predominantly evaporative), which implies Stefan flow with a mean velocity
53 component normal to the surface. Net mass transfer across a surface results in a velocity component
54 normal to the surface, and an associated non-diffusive flux in the direction of mass transfer (Kreith et al.,
55 1999). The existence and relevance of Stefan flow – first derived and described in the 19th century – is
56 certain. Indeed, engineers necessarily account for its role in heat and mass transfer (Abramzon and
57 Sirignano, 1989) when precisely controlling industrial processes that include phase change, such as
58 combustion. For these reasons, it is to be expected that a more accurate means of estimating $w|_0$ for the
59 atmospheric boundary layer can be achieved by rigorous examination of known surface flux densities in
60 the light of physical laws.

61

62 The remaining sections of this work aim to diagnose a defensible lower boundary condition for the
63 vertical velocity ($w|_0$) and to interpret its significance. Section 2 presents the theory, and illustrates types
64 of mass transport and heat exchange in fluids via an example from the liquid phase. In Section 3, an
65 analytical framework is established and conservation of linear momentum is applied to derive $w|_0$ from
66 published magnitudes of surface gas exchanges, demonstrating that it is directly proportional to the
67 evaporative flux density (E), consistent with the findings of Stefan. The derived vertical velocity is seen
68 to be relevant in defining the mechanisms of gas transport, which is not accomplished by diffusion alone
69 – even at the surface interface. Section 4 highlights the need to rectify flux-gradient relationships by
70 taking into account the non-diffusive component of transport; this includes boundary-layer similarity
71 theory and physiological descriptions of stomatal conductance. Thus, the implications of these analyses
72 are broad and interdisciplinary.

73 **2 Theory**

74 The objective of this section is to establish the theoretical bases for the analyses and interpretations that
75 follow. It opens with a list of symbols (Table 1) along with the meaning and S.I. units of each variable
76 represented, and finishes with a summary of the most salient points regarding physical laws and transport
77 mechanisms to be recalled in Section 3.

78 **2.1 Relevant Scientific Laws**

79 **2.1.1 The Law of Conservation of Linear Momentum**

80 The principle of conservation of momentum is most fundamental in physics, more so than even Newton's
81 1st Law (Giancoli, 1984). It defines the momentum of a system of particles as the sum of the momenta of
82 the individual components, and establishes that this quantity is conserved in the absence of a net external
83 force. Accordingly, in atmospheric dynamics (Finnigan, 2009) a system may be defined as the N
84 component gas species comprising a particular mass of air, with a net vertical flux density of

$$85 \quad w\rho = \sum_{i=1}^N w_i\rho_i. \quad (1)$$

86 In Eq. (1), w and ρ represent the vertical velocity and density of air, respectively, while w_i and ρ_i are the
87 properties of component i , whose species flux density is $w_i\rho_i$. For this species i , total transport $w_i\rho_i$ can
88 be attributed to mechanisms that are diffusive (if $w_i \neq w$), non-diffusive (if $w = 0$), or more generally a
89 combination of these two types of transport. Dividing Eq. (1) by the net air density defines the system's
90 vertical velocity as a weighted average of its components (Kowalski, 2012), where the weighting factors
91 are the species' densities.

92 **2.1.2 The 0th Law of Thermodynamics**

93 The 0th Law establishes the temperature as the variable whose differences determine the possibility for
94 heat exchange between thermodynamic systems. For two systems in thermal contact, if they have the
95 same temperature then they are in thermodynamic equilibrium and therefore exchange no heat. If their
96 temperatures differ, then heat will be transferred from the system with the higher temperature to that with
97 the lower temperature. Heat transfer by molecular conduction depends on gradients in the temperature; in
98 compressible fluids like air, however, turbulent diffusion can occur without thermal contact and yet bring
99 about heat transfer as determined by gradients in the potential temperature (Kowalski and Argüeso,
100 2011), accounting for any work done/received during the expansion/compression associated with vertical
101 motions.

102 **2.1.3 Fick's 1st Law of Diffusion**

103 Molecular diffusion has no effect on the net fluid momentum, but "randomly" redistributes fluid
104 components and can cause different species to migrate in different directions, according to component
105 scalar gradients. Regrettably, scientific literature contains inconsistencies regarding the scalar whose
106 gradient determines diffusion in the gas phase (Kowalski and Argüeso, 2011). The proper form of Fick's
107 1st Law for diffusion in the vertical direction is

108 $F_{i,M} = -\rho K \frac{\partial f_i}{\partial z},$ (2)

109 where $F_{i,M}$ is the vertical flux density of species i due to molecular diffusion, which is proportional to the
 110 vertical gradient in that species' mass fraction (f_i ; Bird et al. (2002)), and z is height. Also relevant are the
 111 fluid density (ρ) and molecular diffusivity (K). However, ρ must not be included in the derivative in Eq.
 112 (2), unless for the trivial case where it is constant (as in an incompressible fluid); in compressible media,
 113 gradients in gas density can arise, with no direct relevance to diffusion, due to gradients in pressure or
 114 temperature as described by the Ideal Gas Law. It is relevant to note that Adolf Fick arrived at this law,
 115 not by experimentation, but rather by analogy with Fourier's law for heat conduction (Bird et al., 2002).
 116 By the same analogy, the product of the diffusivity with the scalar gradient in Eq. (2) yields a kinematic
 117 flux, which requires multiplication by the fluid density in order to yield the flux density of interest.

118
 119 Fluxes due to molecular diffusion are referenced to the motion of the fluid's centre of mass, or "mixture
 120 velocity" (Bird et al., 2002). The simplest example to describe this is that of binary diffusion where only
 121 two species compose the fluid, as in the traditional meteorological breakdown of air into components
 122 known as dry air and water vapour. In the case of "static diffusion", the fluid velocity is zero and the mass
 123 flux of one gas species (water vapour) counterbalances that of the other (dry air). When diffusion occurs
 124 in a dynamic fluid (non-zero velocity), then overall transport must be characterized as the sum of
 125 diffusive and non-diffusive components.

126
 127 Turbulent diffusion is analogous to molecular diffusion in the sense that fluid components are randomly
 128 redistributed, with different species migrating as a function of gradients in their mass fractions. The
 129 primary difference is that eddies rather than molecular motions are responsible for mixing, and the eddy
 130 diffusivity (the value of K in Eq. (2), describing "K-theory" (Stull, 1988)) is a property of the flow rather
 131 than the fluid. The Reynolds number describes the relative importance of molecular and turbulent
 132 diffusion, which are otherwise indistinct with respect to the analyses that follow, and will simply be
 133 grouped and referred to as "diffusive transport".

134

135 **2.2 Transport processes**

136 In this section, two case studies from the liquid phase will help identify and define non-diffusive and
 137 diffusive types of transport, as well as their scalar source/sink determinants. Let us consider the case of
 138 freshwater ($35 \cdot 10^{-5}$ mass fraction of salt) with constant temperature and composition flowing through a
 139 tube into the bottom of a pool (Figure 1) of salinity specified according to the two case scenarios defined
 140 below. Considering only flow within the tube (at point 1), whether laminar or turbulent, it clearly realizes
 141 non-diffusive transport of salt, since the salt has no particular behaviour with respect to the fluid, but
 142 simply goes with the flow. There are no scalar gradients within the tube, and so there is neither diffusion
 143 nor advection. Let us now describe diffusive transport processes within the pool (at point 2), and the
 144 nature (whether absolute or relative) of the relevant fluid properties whose gradients determine them by
 145 defining sources/sinks, using two illustrative case scenarios.

146

147 The temperature is constant in time and space, but other *characteristics of the two case scenarios* are
148 chosen to elucidate the relationship between diffusive transport processes and scalar gradients:

149 1) *Due to surface evaporation that balances the mass input from the tube, the pool mass is constant; the*
150 *water is maintained isothermal by surface heating that supplies the (latent) energy for evaporation.*
151 *Initially (t_0) the pool has zero salt mass, but salinity increases constantly, equalling that of the tube*
152 *water at some moment (t_{eq}) and rising by another two orders of magnitude to reach that of sea water*
153 *($35 \cdot 10^{-3}$) by the end of the scenario (t_f). This case is of interest from both (a) salt/solute and (b)*
154 *thermodynamic points of view:*

155 a) In solute terms, the tube represents a source of (absolute) salt to the pool, but not always of
156 (relative) salinity. Initially (t_0), the water from the tube is more saline than that in the pool, such
157 that non-diffusive and diffusive transport processes operate in tandem to transport salt from the
158 tube upward into the pool; at this moment, the tube is a source of salinity. Salinity advection,
159 defined as the negative of the inner product of two vectors (the velocity with the salinity
160 gradient, with opposite signs), is then positive. Ultimately however (at $t > t_{eq}$), the water in the
161 pool is more saline than that entering from the tube, such that non-diffusive and diffusive salt
162 transport are in opposite directions; then the tube dilutes the pool and is a salinity sink, but still a
163 salt source. Salinity advection at t_f is negative. The pool continues to gain salinity after t_{eq} ,
164 despite the diluting effects of the tube, due to the concentrating effects of evaporation, which is
165 the ultimate source of salinity. This distinction matters because the gradients that drive advection
166 and diffusion are those in salinity, a relative (not absolute) salt measure. At t_f , the diffusive
167 salinity fluxes are oriented against the flow within the pool (downward, and radially inward
168 towards the diluting tube, despite its being a net salt source). By contrast, non-diffusive transport
169 always goes with the flow, and accounts for continued upward and outward salt transport,
170 increasing the salt content at the surface.

171 b) Although thermodynamically trivial – with no heat exchanges whatsoever within the water as
172 determined by the 0th Law – this case nonetheless illustrates the nature of the scalars that
173 determine heat transfer by advection and diffusion (conduction). The “heat content” of the pool
174 decreases as it becomes more and more saline, due to the inferior heat capacity of saltwater
175 versus freshwater. Similarly, salt diffusion/advection is initially upward/positive but ultimately
176 downward/negative, yet the corresponding implications regarding heat content fluxes say
177 nothing about the transfer of heat. The point here is that the dynamics of the heat content must
178 not be interpreted in terms of heat fluxes, which was done by Finnigan et al. (2003). For this
179 reason, meteorologists correctly define “temperature advection” (Holton, 1992) based the
180 thermodynamic relevance of gradients in the variable singled out by the 0th Law.

181

182 2) *Let us now specify that the water in the pool has the same (freshwater) salinity as that coming from*
183 *the tube ($35 \cdot 10^{-5}$). If we furthermore remove both surface evaporation and heating from scenario (1),*
184 *then the temperature remains constant and the salinity corresponds uniformly to that of freshwater,*
185 *but the pool accumulates mass. In this case, there are convergences in the non-diffusive transports of*
186 *water, salt, and heat content: fluxes into the pool are positive, while fluxes out are null. However,*

187 there are no gradients in temperature or salinity, and so there is neither diffusion nor advection in this
188 scenario. The pool does gain volume (depth) but this is only because the fluid under consideration is
189 incompressible. By contrast, for the gas phase, accumulation of absolute quantities – such as air and
190 trace constituent mass, and heat content – can occur in a constant volume context (e.g., “at a point”,
191 in an Eulerian fluid specification) due to convergent, non-diffusive transport that defines
192 compression. In the pool, diffusion and advection are clearly null because they are determined by
193 gradients in the relative trace gas amount – the mass fraction –, a variable of essential utility for the
194 gas phase because it is immune to the effects of compression.

195

196 **2.3 An advection-diffusion synopsis**

197 The analyses that follow rely on the succeeding key points drawn from sections 2.1 and 2.2. Advection
198 and diffusion depend on gradients in scalars whose nature is relative rather than absolute. In
199 incompressible thermodynamics, the relevant gradients are those in the temperature, and not the heat
200 content. For trace constituents, the relevant scalar is the mass fraction (e.g., salinity) and not the species
201 density. Advection and diffusion are otherwise physically very distinct. Like non-diffusive transport,
202 diffusion is a vector whose vertical component is of particular interest in the context of surface-
203 atmosphere exchange. By contrast, advection is a scalar; for some arbitrary quantity ξ , it is defined as the
204 negative of the inner product $\mathbf{v} \cdot \nabla \xi$, where \mathbf{v} is the fluid velocity and ∇ is the gradient operator. Thus
205 advection, unlike diffusion, is not a form of transport, but rather a consequence of differential transport.

206

207 The scenarios depicted above correspond to the incompressible case (liquid). When the effects of
208 compressibility are irrelevant, it can be convenient to add the incompressible form of the continuity
209 equation ($\nabla \cdot \mathbf{v} = 0$) to advection yielding $-\nabla \cdot \xi \mathbf{v}$, the convergence of a kinematic flux. This is called the
210 “flux form” of advection. For a compressible medium such as the atmosphere, however, if ξ is taken to
211 represent some “absolute fluid property such as the (gas) density” (Finnigan et al., 2003), then the
212 transformation of advection into flux form cannot be justified (Kowalski and Argüeso, 2011), since using
213 the incompressible form of the continuity equation leads to unacceptable errors in conservation equations
214 for boundary-layer control volumes (Kowalski and Serrano-Ortiz, 2007). By contrast, the expression of
215 advection in flux form can be valid if the scalar ξ is carefully chosen for its immunity to the effects of
216 compression, as is the case for the mass fraction. These generalizations regarding the nature of transport
217 by non-diffusive and diffusive mechanisms, and also the nature of advection, will now be applied to the
218 case of vertical transport very near the surface and the mechanisms that participate in surface exchange,
219 after first deriving the boundary condition $w|_0$.

220 **3 Analysis**

221 **3.1 Framework**

222 The analysis will focus on a system defined as a mixture of gas molecules of different species, whose
223 momentum will be examined. The system’s mass is defined (Table 2) by gas components in a ratio that

224 corresponds quite closely to that of the atmosphere (Wallace and Hobbs, 2006) but updated to more
225 closely reflect actual atmospheric composition. At a representative ambient temperature ($T = 298$ K) and
226 pressure ($p = 101325$ Pa), the many millions of molecules forming this system occupy a volume of 10^{-15}
227 m^3 with 70% relative humidity. The system geometry will be specified in four different ways, according
228 to the different spatial scales for which $w|_0$ is to be described:

- 229 A. At the synoptic scale, the volume occupied by the system is a lamina of depth $\delta z \sim 10^{-27}$ m,
230 bounded above and below by constant geopotential surfaces, with horizontal dimensions (Δx and
231 Δy) on the order of 10^6 m. The fact that δz is thinner than the dimension of a molecule matters
232 not at all when classifying any and all molecules whose centres of mass (points, with neither size
233 nor dimension) occupy the lamina as belonging to the volume;
- 234 B. At the micrometeorological scale, the volume overlies a flat surface and is shaped as a
235 rectangular lamina of depth $\delta z \sim 10^{-21}$ m, with horizontal dimensions (Δx and Δy) of 10^3 m;
- 236 C. At the leaf scale, the volume is a rectangular lamina of depth $\delta z \sim 10^{-11}$ m, with horizontal
237 dimensions (Δx and Δy) of 10^{-2} m; and
- 238 D. At the microscopic scale of plant stomata, the volume is a cube with $\Delta x = \Delta y = \delta z = 10^{-5}$ m. For
239 the purpose of transitioning between the leaf and microscopic scales, plant pores are assumed to
240 occupy a stomatal fraction σ of the leaf surface and yet accomplish all gas exchange, with the
241 remaining fraction $(1-\sigma)$ occupied by a cuticular surface whose gas exchange is assumed to be
242 null (Jones, 1983).

243 Independent of scale, the base height $z|_0$ of the volume is the lowest for which only air – and neither
244 ocean wave nor land surface element – occupies the volume. The land/ocean/leaf surface will be assumed
245 to be static (i.e., its vertical velocity is zero), impenetrable to the wind (explicitly neglecting ventilation of
246 air-filled pore space), smooth, level and uniform, all for the sake of simplicity. The temporal framework
247 for the analysis is instantaneous, with no need to choose between Eulerian and Lagrangian fluid
248 specifications.

249

250 The direction of momentum transport to be examined is vertical, meaning perpendicular to constant
251 geopotential surfaces and therefore to the underlying surface. At the stomatal scale, the stoma to be
252 examined is situated on the upper side of a flat, horizontal leaf; water vapour exiting the stomatal aperture
253 during transpiration therefore has a positive vertical velocity. These analyses can be generalized to
254 sloping surfaces and/or stomata on the underside of leaves, simply by referring to the “surface-normal”
255 rather than “vertical” velocity. Hereinafter, however, the term “vertical” will be employed for
256 conciseness.

257

258 **3.2 The vertical velocity at the surface boundary**

259 Knowledge regarding surface exchange (gas flux densities) has advanced to the point where the boundary
260 condition for the vertical velocity ($w|_0$) can be estimated from conservation of linear momentum –
261 applying Eq. (1) to the system defined in Table 2 –, and vastly simplified to a simple function of the
262 evaporation rate (E). The species flux densities ($w_i \rho_i$) within the system represent the surface exchanges

263 of the corresponding gas species (i). Scale analysis of surface gas exchange magnitudes, published from
 264 investigations at a particularly well-equipped forest site in Finland (Table 3), reveals that for the water
 265 vapour species ($i=4$), the flux density ($E = w_4 \rho_4$) is orders of magnitude larger than both the flux density
 266 of any dry air component species and even the net flux density of dry air. Such dominance by water
 267 vapour exchanges is representative of most surfaces worldwide. This is especially so because the two
 268 largest dry air component fluxes are opposed, with photosynthetic/respiratory CO_2 uptake/emission
 269 largely offset by O_2 emission/uptake (Gu, 2013). Hence, following tradition in micrometeorology (Webb
 270 et al., 1980), dry air exchange can be neglected, allowing the elimination from Eq. (1), when applied at
 271 the surface, of all species flux densities except for that of water vapour (H_2O ; $i=4$). Therefore, net air
 272 transfer across the surface can be approximated very accurately as

$$273 \quad w|_0 \rho|_0 = w_4|_0 \rho_4|_0 = E, \quad (3)$$

274 where $w_4|_0$ and $\rho_4|_0$ are the H_2O species velocity and density at the surface. Equation (3) states that, at
 275 the surface, the net vertical flux density of air is equal to the net vertical flux density of water vapour,
 276 which is the evaporation rate. Solving this for $w|_0$ allows estimation of the lower boundary condition for
 277 the vertical velocity as

$$278 \quad w|_0 = \frac{E}{\rho_4|_0}. \quad (4)$$

279
 280 The representative evaporation rate prescribed in Table 3 and vertical velocity resulting from eq. (4) are
 281 valid for most of the scales defined above. Thus, the boundary condition $w|_0$ is valid for the synoptic
 282 scale (notwithstanding vertical motion aloft, such as subsidence), for the micrometeorological scale, and
 283 even for the leaf scale. In the context of scale analysis, leaves may be approximated as having equal area
 284 as the underlying surface (i.e., a unit leaf area index, or LAI=1), and equal evaporation rates as the surface
 285 in general. This latter assumption does not neglect soil evaporation, but only excludes the possibility that
 286 it dominate leaf evaporation by an order of magnitude. Thus, it will be assumed here that the assumed
 287 evaporation rate and derived vertical velocities are equally valid at synoptic (A), micrometeorological
 288 (B), and leaf (C) scales. The order of magnitude is different, however, at the microscopic (D) scale. To
 289 show this, it will be assumed here that all leaf evaporation (or transpiration) occurs through the small
 290 fraction of the leaf that is stomatal (σ), such that both the stomatal evaporative flux density and the lower
 291 boundary condition for the vertical velocity ($w|_0$) are a factor $1/\sigma$ greater than that at larger scales.
 292 Independent of scale, Eq. (4) states that, for a positive evaporation rate, the boundary condition for the
 293 vertical velocity is non-zero and upward.

294
 295 Given that the surface boundary is static, it may well be asked why there is a non-zero boundary condition
 296 for the vertical velocity of air. The answer is that evaporation induces a pressure gradient force that
 297 pushes air away from the surface. Evaporation into air increments the water vapour pressure and thereby
 298 the total pressure, according to Dalton's law. If evaporation were to proceed until achieving equilibrium,
 299 the pressure added by evaporation would correspond to the saturation vapour pressure (e_s ; Figure 2),
 300 whose temperature dependency has been quantified empirically and is described by the Clausius-

301 Clapeyron relation. It is this evaporation-induced pressure gradient force that pushes the manometer in
302 Fig. 2 to its new position, and similarly that drives winds away from the surface.

303

304 Although this upward air propulsion occurs at the surface, air velocities are generally upward throughout
305 the boundary layer in a climatological context. Indeed, the dominant role of water vapour in determining
306 the net vertical momentum of air is a general feature of the troposphere. In the context of the
307 hydrological cycle, water vapour is transported from the surface where it has an evaporative source, to
308 further aloft where clouds develop via processes that act as water vapour sinks: condensation and vapour
309 deposition onto ice crystals (or ice nuclei). In terms of total water, upward transport in the gas phase is
310 offset, over the long term, by downward transport in liquid and solid phases (e.g., rain and snow); unlike
311 the water vapour flux, however, precipitation does not directly define air motion. It is true that downward
312 water vapour transport occurs during dewfall – with surface condensation, as described by Eq. (4) with a
313 negative evaporation rate ($E < 0$) –, but this plays a minor role in the global water balance. Generally, the
314 relative magnitudes of gas exchanges used for the scale analysis in Table 3 are representative throughout
315 most of the troposphere, with upward water vapour flux densities dominating those of other gases in the
316 vertical direction. In the surface layer, sometimes termed the “constant flux layer” (Dyer and Hicks,
317 1970), Eq. (4) can be extrapolated away from the surface under steady-state conditions to yield

$$318 \quad w = \frac{E}{\rho}. \quad (5)$$

319

320 **3.3 Mechanisms of gas transport at the surface**

321 Non-zero vertical momentum in the lower atmosphere and right at the surface boundary – dominated by
322 the flux density of water vapour and generally upward due to evaporation – means that diffusion is not the
323 lone relevant transport mechanism that participates in surface exchange, as has been generally supposed.
324 This is true for all atmospheric constituents, and not only for water vapour; over an evaporating surface,
325 any molecule undergoing collisions with its neighbours does not experience a random walk (a
326 characteristic of static diffusion), but rather tends to be swept upward with the flow. The upward air
327 current similarly wafts aerosol particles, although these may move downwards if their fall velocities
328 exceed the upward air motion. The upward flow velocity is rather small – just $31 \mu\text{m s}^{-1}$ for the conditions
329 specified above and the evaporation rate of Table 3, according to Eqs. (4) and (5). It does not exclude the
330 possibility of diffusive transport in any direction, but does imply a relevant, non-diffusive component of
331 transport for any gas, whose magnitude is not related to that gas’s scalar gradient.

332

333 The non-diffusive flux density of species i can be expressed as

$$334 \quad F_{i,non} = w\rho_i, \quad (6)$$

335 and when substituting for w from Eq. (5) this becomes

$$336 \quad F_{i,non} = Ef_i, \quad (7)$$

337 i.e., the product of the evaporation rate and the species mass fraction. Examination of its magnitude near
338 the surface for different gases will now show that, while this is often small in comparison with the
339 diffusive component, it is not negligible in every case, depending on the magnitudes of the mass fraction
340 and surface exchange for the gas considered.

341

342 Interpreting decomposed transport is simplest when examining a gas whose surface exchange is very well
343 known, such as the null value for inert Argon (Ar) that constitutes ca. 1.3% of dry atmospheric mass
344 (Wallace and Hobbs, 2006). Considering the state variables defined by Table 2 and the evaporation rate
345 of Table 3, Eq. (7) indicates $458 \mu\text{g m}^{-2} \text{s}^{-1}$ (a molar flux density of $11.6 \mu\text{mol m}^{-2} \text{s}^{-1}$) of upward, non-
346 diffusive Ar transport ($F_{3,\text{non}}$). To comprehend this, it helps to recall that the constant addition of H₂O
347 dilutes dry air at the surface and promotes its downward diffusion. For a null net flux of inert Ar to exist,
348 downward diffusion of this dry air component must exactly cancel the upward non-diffusive transport,
349 and therefore is $458 \mu\text{g m}^{-2} \text{s}^{-1}$ for the state and evaporative conditions specified above. These opposing
350 non-diffusive and diffusive Ar transport processes are quite analogous to case scenario 1 of Section 2.2, at
351 the instant t_f when the fluid emitted into the pool has a diluting effect. Such dual transport mechanisms
352 are also relevant for vital gases, with different transport directions and degrees of relevance, depending on
353 the density and flux density of the gas in question.

354

355 For H₂O, the two types of gas transport mechanisms operate in tandem, with the non-diffusive component
356 contributing a fraction of upward H₂O transport that, according to Eq. (7), is exactly the water vapour
357 mass fraction or specific humidity (Wallace and Hobbs, 2006)

$$358 \quad q \equiv f_4 \equiv \frac{\rho_4}{\rho}. \quad (8)$$

359 This is just 2% for the state conditions previously specified, but can approach 5% for very warm
360 evaporating surfaces and/or high-altitude environments. The breakdown of H₂O transport into diffusive
361 and non-diffusive components is analogous to case scenario 1 of Section 2.2 at an instant prior to t_{eq} when
362 the fluid introduced to the pool is highly concentrated, in comparison with the fluid already in the pool. In
363 any case, non-diffusive H₂O transport is generally secondary to diffusive transport, but its neglect in an
364 ecophysiological context can lead to larger relative errors, as will be shown in Section 4.

365

366 For CO₂, which usually migrates downward during evaporative conditions because of photosynthetic
367 uptake, upward transport of a non-diffusive nature is even more relevant, opposing the downward flux
368 due to diffusion. To see this, let us examine the typical gas transport magnitudes of Table 2 and the
369 atmospheric state conditions specified above. According to Eq. (7), non-diffusive CO₂ transport ($F_{5,\text{non}}$) is
370 then $21.5 \mu\text{g m}^{-2} \text{s}^{-1}$ (a molar flux density of $0.49 \mu\text{mol m}^{-2} \text{s}^{-1}$) in the upward direction, requiring that
371 downward CO₂ diffusion be $109.5 \mu\text{g m}^{-2} \text{s}^{-1}$ in order to yield $88 \mu\text{g m}^{-2} \text{s}^{-1}$ of net surface uptake; if not
372 accounting for the non-diffusive resistance to net transport, the CO₂ diffusivity would be underestimated
373 by ca. 20%. The case of CO₂ uptake is not analogous to any pool/tube scenario in Figure 1. However,
374 different conditions with equal evaporation ($E = 36 \text{ mg m}^{-2} \text{s}^{-1}$) and CO₂ emission in the amount of 21.5
375 $\mu\text{g m}^{-2} \text{s}^{-1}$ (by respiration, for example) would correspond to the case of zero CO₂ diffusion (as at the

376 instant t_{eq}), since the CO_2 mass fractions of both the atmosphere and the gas mixture emitted by the
377 surface are identical. Viewed in the traditional diffusion-only paradigm, such a situation involving a net
378 flux but no gradient ($F_3 = F_{3,non}$) would require a physically absurd infinite diffusivity. At this same
379 evaporation rate, but with lower CO_2 emission, diffusion of CO_2 would be downward, towards the surface
380 which is a source of CO_2 but a sink of the CO_2 mass fraction (analogous to salinity in case scenario 1 of
381 Section 2.2 at some instant between t_{eq} and t_f when the fluid emitted to the pool has a diluting effect).
382 Whatever the direction of net CO_2 transport, these case examples demonstrate the need for sometimes
383 substantial rectifications to flux-gradient relationships – whether expressed as a conductance, resistance,
384 deposition velocity, or eddy diffusivity (K-theory), – when correctly accounting for non-diffusive
385 transport.

386 **4 Discussion**

387 Relevant transport of a non-diffusive nature implies the need to revise the basis of flux-gradient theory,
388 both in the boundary layer and also at smaller scales regarding gas transfer through plant pores. One of
389 the key goals of micrometeorology has been the derivation of the vertical transports of mass, heat, and
390 momentum from profiles of wind speeds and scalar variables in the boundary layer (Businger et al.,
391 1971). The analyses above elucidate how gradients relate to only the diffusive components of such
392 exchanges. Therefore, non-diffusive flux components must be subtracted out in order to characterize
393 turbulent transport in terms of eddy diffusivities, a key goal of Monin-Obukhov Similarity Theory
394 (Obukhov, 1971). Perhaps more important is the need to distinguish between non-diffusive and diffusive
395 transport mechanisms prior to assessing molecular diffusivities (conductances).

396

397 When Eq. (3) is applied at the stomatal apertures where virtually all plant gas exchanges occur, it is
398 revealed that jets of air escape from these pores during transpiration. In the context of the scale analysis
399 begun in Section 3.2, it is appropriate to note that even fully open stomata occupy just 1% of leaf area
400 (Jones, 1983), leaving 99% cuticular and inert with regard to vital gas exchanges ($\sigma = 0.01$). As noted in
401 Section 3.2, this means that for the microscopic scale (D ; Section 3.1) of the stomatal aperture, both the
402 local evaporative flux density (E) and therefore the lower boundary condition for the vertical velocity
403 ($w|_0$) predicted by Eq. (4) are two orders of magnitude greater than the $31 \mu m s^{-1}$ estimated above. In
404 other words, a typical average airspeed exiting a stomatal aperture is $3.1 mm s^{-1}$. For non-turbulent flow
405 through a cylindrical tube/aperture (i.e., Poiseuille flow), the velocity at the core of such an air current is
406 twice as large. If a characteristic time scale is defined for air blowing through stomata as the ratio of a
407 typical stomatal aperture diameter (ca. $6 \mu m$) to this core velocity, it is found to be of order 10 ms,
408 illustrating that air is expelled from plants in the form of “stomatal jets”. Non-diffusive gas transport by
409 such airflow exiting stomata – assisting with water vapour egress but inhibiting CO_2 ingress – has been
410 previously conceived.

411

412 The concept of net motion and consequent non-diffusive transport out of stomata is not new, but has been
413 disregarded by plant ecologists. Parkinson and Penman (1970) put forth that the massive water vapour

414 flux from transpiration implies an outbound air current as a background against which diffusion operates.
415 Regrettably, however, their interpretation has largely been forgotten, having been refuted in an analysis
416 (Jarman, 1974) that incorrectly assumed “no net flow of air” – disregarding conservation of momentum –
417 and yet seems to have gained acceptance (von Caemmerer and Farquhar, 1981). Similarly, Leuning
418 (1983) recognized the relevance of non-diffusive transport and furthermore identified excess pressure
419 inside the stomatal cavity as the impetus for the outward airstream (which he termed “viscous flow”), but
420 had little impact on the mainstream characterization of stomatal conductance. Rather, important aspects
421 of ecophysiology continue to hinge upon the assumption that diffusion alone transports vital gases
422 through plant pores, disregarding both the above-mentioned studies and more importantly the fact that gas
423 transport mechanisms through such apertures were accurately described by one of the great physicists of
424 the 19th century.

425
426 Because Josef Stefan helped substantially to establish the fundamentals of classical physics, his name is
427 often mentioned in the same breath as those of Boltzmann (regarding blackbody radiation) and Maxwell
428 (for diffusion). However, his work in the latter regard has been broadly ignored by scientists studying gas
429 exchanges through plant stomata. Stefan's study of evaporation from the interior of a narrow, vertical
430 cylinder with vapour transport into an overlying, horizontal stream of air is of particular relevance to the
431 discipline of ecophysiology. He determined that this is not a problem of “static diffusion”, but rather
432 includes an element of non-diffusive transport due to a mean velocity in the direction of the vapour flux,
433 induced by evaporation and now commonly known as Stefan flow. Engineers know this history, refer to
434 such a scenario as a Stefan tube (Lienhard and Lienhard, 2000), and routinely reckon transport by Stefan
435 flow in addition to that caused by diffusion. Such accounting is necessary for precise control in industrial
436 applications such as combustion, and is described in many chemical engineering texts (Kreith et al., 1999;
437 Lienhard and Lienhard, 2000; Bird et al., 2002). The phenomenon of transpiration through a stoma is a
438 reasonable proxy for a Stefan tube, the main difference being that evaporation in the Stefan tube depletes
439 the pool of evaporating liquid, whose surface therefore recedes downward. By contrast, the evaporating
440 water in the stomatal cavity is continually replenished by vascular flow from within the plant; if anything,
441 this reinforces the magnitude of the upward vertical air velocity, in comparison with the Stefan tube,
442 consistent with that derived from momentum conservation as in Eqs. (4) and (5).

443
444 Non-diffusive transport by Stefan flow has implications for defining key physiological parameters,
445 greater than the percentages of CO₂ and water vapour transport calculated above. Plant physiologists have
446 postulated that stomata act to maximise the ratio of carbon gain to water loss (Cowan and Farquhar,
447 1977) or water use efficiency (WUE), an ecosystem trait that constrains global biogeochemical cycles
448 (Keenan et al., 2013). In formulating this parameter, presuming molecular diffusion to be the lone
449 transport mechanism, the water vapour conductance is usually taken as 1.6 times that of CO₂ (Beer et al.,
450 2009), based on the ratio of their diffusivities – the inverse of the square root of the ratio of their
451 molecular masses, according to Graham's law. Such an assumption underlies the very concept of stomatal
452 control (Jones, 1983), but neglects the role of non-diffusive transport for both gases. Net momentum
453 exiting stomata both expedites water vapour egress and retards CO₂ ingress, versus the case of static

454 diffusion, in each case acting to reduce the WUE. Importantly, water vapour transport by stomatal jets
455 depends not only on physiology but also physically on the state variable q , according to Eq. (8).
456 Consistent with the determinants of q , as the temperature of a (saturated) stomatal environment increases,
457 even for a constant stomatal aperture, the WUE is reduced, wresting some control over gas exchange rates
458 from the plant. Perhaps equally importantly, opposition to CO₂ uptake by stomatal jets also should be
459 considered when modelling the most fundamental of biological processes, namely photosynthesis.

460

461 Accurate modelling of primary production in plants may require a fuller description of stomatal transport
462 mechanisms, including non-diffusive expulsion by jets. The partial pressure of CO₂ inside the stomata is a
463 key input parameter for the classic photosynthesis model (Farquhar et al., 1980), but is never directly
464 measured. Rather, it must be inferred from gas exchange measurements and assumptions about the
465 relative conductance of water vapour and CO₂, as described above. The amendment of such calculations
466 to account for non-diffusive transport of both CO₂ and H₂O should help to improve the accuracy of
467 physiological models.

468

469 As a final note regarding ecophysiology, studies of plant functioning conducted using alternative gas
470 environments should be interpreted with care. Stomatal responses to humidity variations have been
471 studied in several plant species using the He:O₂ gas mixture termed “helox” (Mott and Parkhurst, 1991).
472 In the context of conservation of linear momentum, it is relevant that the effective molecular weight of
473 helox is just 29% that of dry air. Under equal conditions of temperature and pressure, helox has far less
474 density, and so during transpiration both $w|_0$ from Eq. (4) and the non-diffusive component of stomatal
475 transport from Eq. (7) are 3.5 times greater than in air. The validity of helox for characterizing natural
476 plant functioning is thus dubious due to its low inertia versus that of air.

477 **Conclusions**

478 Evaporation (E) is the dominant surface gas exchange, and forces net upward momentum in the surface
479 layer such that the lower boundary condition for the vertical velocity is $w|_0 = \frac{E}{\rho|_0}$, where $\rho|_0$ is the air
480 density at the surface. This non-zero vertical velocity describes Stefan flow and implies gas exchange of a
481 non-diffusive nature, which must be extracted from the net transport of any gas prior to relating that gas’s
482 resultant diffusive transport component to scalar gradients, as in Monin-Obukhov Similarity Theory. Such
483 correction of flux-gradient theory is of particular import for descriptions of gas exchange through plant
484 stomata, which should be amended to account for non-diffusive transport by “stomatal jets” that help
485 expel water vapour but hinder the ingress of CO₂

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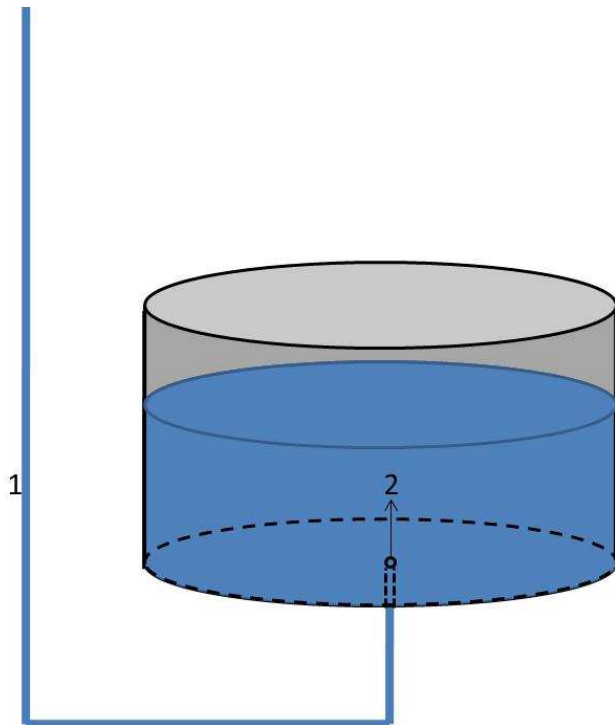
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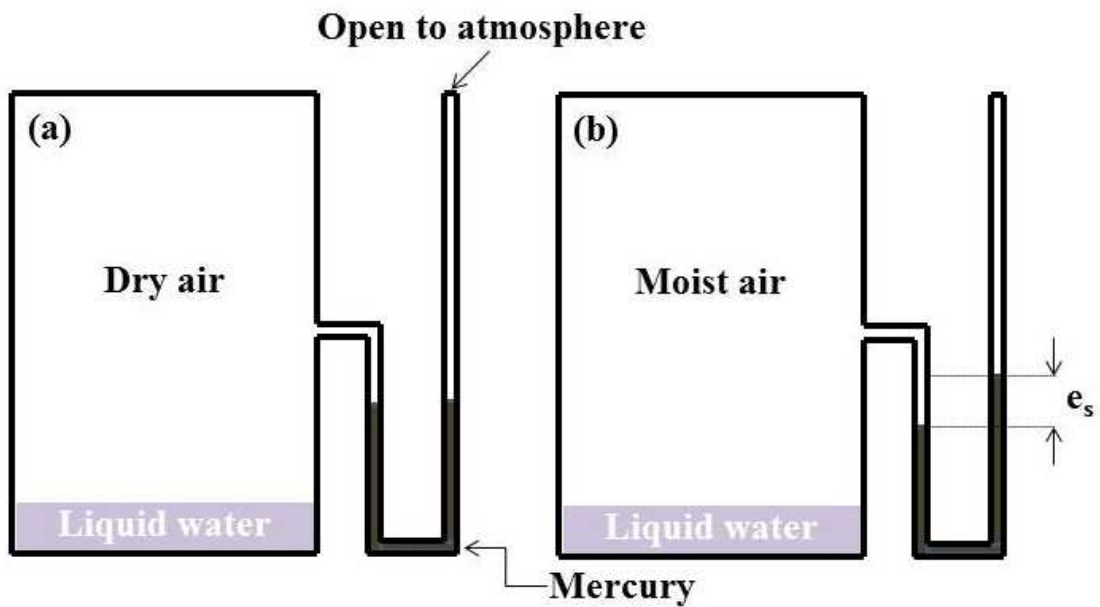
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Figure 1: A pool of water being fed from below by a tube. The points indicate water (1) in the tube, and (2) in the pool. The arrow indicates the direction of flow.



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Figure 2: Illustration of evaporation incrementing air pressure. Chamber air evolves from (a) dry air initially at atmospheric pressure; to (b) moist air at a pressure that has risen by the partial pressure of water vapour, ultimately at equilibrium (saturation vapour pressure, e_s). The force generated by evaporation propels the mercury in the manometer from its initial position.

588 **Table 1: List of symbols, with their meanings and units.**

Symbol	Variable represented	S.I. Units	Tensor Order
General Variable Representations			
ξ	An arbitrary magnitude (can represent any scalar variable)	Depends on ξ	0 (scalar)
ξ_i	The magnitude of arbitrary variable ξ for gas species i	Depends on ξ	0 (scalar)
$\nabla\xi$	The spatial gradient in arbitrary variable ξ	Depends on ξ	1 (vector)
$[\xi]_0$	The lower boundary condition for arbitrary variable ξ	Depends on ξ	0 (scalar)
Specific Variable Representations			
$\Delta x, \Delta y$	Horizontal dimensions of an analytical volume	m	0 (scalars)
δz	Vertical dimension (thickness) of an analytical volume	m	0 (scalar)
E	Evaporative flux density across a horizontal surface	$\text{kg m}^{-2} \text{s}^{-1}$	0 (component)
e_s	Saturation vapour pressure	Pa	0 (scalar)
f	Mass fraction	Non-Dimensional	0 (scalar)
F_i	Vertical flux density of gas species i	$\text{kg m}^{-2} \text{s}^{-1}$	0 (component)
$F_{i,\text{non}}$	Non-diffusive component of F_i	$\text{kg m}^{-2} \text{s}^{-1}$	0 (component)
i	Index for counting gas species (as in Table 2)	-	0 (scalar)
K	Molecular diffusivity	$\text{m}^2 \text{s}^{-1}$	0 (scalar)
LAI	Leaf area index	Non-Dimensional	0 (scalar)
p	Pressure	Pa	0 (scalar)
q	Specific humidity	Non-Dimensional	0 (scalar)
ρ	Air density	kg m^{-3}	0 (scalar)
σ	Stomatal fraction of leaf area	Non-Dimensional	0 (scalar)
T	Air temperature	K	0 (scalar)
t	Time	s	0 (scalar)
t_0	Initial instant of a case scenario	s	0 (scalar)
t_{eq}	Equilibrium instant of a case scenario	s	0 (scalar)
t_f	Final instant of a case scenario	s	0 (scalar)
\mathbf{v}	Air velocity	m s^{-1}	1 (vector)
w	Vertical component of \mathbf{v}	m s^{-1}	0 (component)
WUE	Water use efficiency	Non-dimensional	0 (scalar)
z	Height above the surface	m	0 (component)

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590

591 **Table 2: Gas components comprising the system to be examined, and their masses.**

<i>i</i>	Gas	Mass (kg)
1	Nitrogen (N ₂)	$9.14 \cdot 10^{-16}$
2	Oxygen (O ₂)	$2.80 \cdot 10^{-16}$
3	Argon (N ₂)	$1.56 \cdot 10^{-17}$
4	Water vapour (H ₂ O)	$1.61 \cdot 10^{-17}$
5	Carbon dioxide (CO ₂)	$7.36 \cdot 10^{-19}$
6	Methane (CH ₄)	$1.14 \cdot 10^{-21}$
7	Nitrous oxide (N ₂ O)	$5.70 \cdot 10^{-22}$
8	Ozone (O ₃)	$4.01 \cdot 10^{-23}$

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593

594 **Table 3: The first six air components by their surface exchange scale magnitude, and the net exchange of air as**
 595 **the sum of these flux densities. Representative surface exchanges are taken from the Finnish boreal forest site**
 596 **(Suni et al., 2003; Aaltonen et al., 2011). The O₂ exchange rate assumes 1:1 stoichiometry with CO₂.**

gas	Typical mass flux, F_i (mg m ⁻² s ⁻¹)	Corresponding molar flux (mmol m ⁻² s ⁻¹)	Source	<i>i</i>
H ₂ O	36	2	(Suni et al., 2003)	4
CO ₂	-0.088	-0.002	(Suni et al., 2003)	5
O ₂	0.064	0.002	(Gu, 2013)	2
CH ₄	-0.000032	-0.000002	(Aaltonen et al., 2011)	6
O ₃	-0.0000096	-0.0000002	(Suni et al., 2003)	8
N ₂ O	0.00000088	0.00000002	(Aaltonen et al., 2011)	7
Air	35.98	-	This study	-

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