



1 The boundary condition for the vertical velocity and its 2 interdependence with surface gas exchange

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8 **Abstract.** The law of conservation of linear momentum is applied to surface gas exchanges, employing
9 scale analysis to diagnose the vertical velocity (w) in the boundary layer. Net upward momentum in the
10 surface layer is forced by evaporation (E) and defines non-zero vertical motion, with a magnitude defined
11 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
12 boundary condition is $w|_0 = \frac{E}{\rho_0}$. This Stefan flow velocity implies upward transport of a non-diffusive
13 nature that is a general feature of the troposphere but is of particular importance at the surface, where it
14 assists molecular diffusion with upward gas migration (of H₂O, e.g.) but opposes that of downward-
15 diffusing species like CO₂ during daytime. The definition of flux-gradient relationships (eddy
16 diffusivities) requires rectification to exclude non-diffusive transport, which does not depend on scalar
17 gradients. At the microscopic scale, the role of non-diffusive transport in the process of evaporation from
18 inside a narrow tube – with vapour transport into an overlying, horizontal air stream – was described long
19 ago in classical mechanics, and is routinely accounted for by chemical engineers, but has been neglected
20 by scientists studying stomatal conductance. Correctly accounting for non-diffusive transport through
21 stomata, which can appreciably reduce net CO₂ transport and marginally boost that of water vapour,
22 should improve characterizations of ecosystem and plant functioning.

23

24 1 Introduction

25 The vertical velocity (w) is a key variable in the atmospheric sciences, whose precise diagnosis is
26 essential for numerous applications in meteorology. Above the boundary layer, the weather is largely
27 determined by adiabatic adjustments to vertical motion that is slight compared to horizontal winds. Closer
28 to the surface, even a tiny w can result in relevant transport; for example, in a typical boundary layer –
29 with representative temperature ($T = 298\text{K}$), pressure ($p = 101325\text{ Pa}$), and CO₂ mass fraction (607 mg
30 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
31 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
32 anemometry cannot resolve such miniscule airflow (Lee, 1998), and generally w is immensurable at many
33 scales so that it must be derived from other variables (Holton, 1992). Such diagnostic estimation is
34 traditional in synoptic meteorology, but has been developed less rigorously near the surface boundary.

35



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

43

44 Micrometeorologists have made presuppositions regarding $w|_0$ without formal justification and in
45 contradiction to deductions from classical mechanics. The traditional hypothesis about near-surface winds
46 is that they flow parallel to underlying terrain (Kaimal and Finnigan, 1994; Wilczak et al., 2001) and
47 vanish at the surface (Arya, 1988), implying $w|_0 = 0$. This assumption underlies many derivations and
48 abets the prevailing belief that vertical exchanges are accomplished purely by molecular diffusion within
49 a millimeter of the surface (Foken, 2008), or purely by turbulent diffusion at heights of meters or more
50 within the atmospheric boundary layer. However, such a premise is inconsistent with the fact of net
51 surface gas exchange (predominantly evaporative), which implies Stefan flow with a mean velocity
52 component normal to the surface.

53

54 Net mass transfer across a surface results in a velocity component normal to the surface, and an
55 associated non-diffusive flux in the direction of mass transfer (Kreith et al., 1999). The existence and
56 relevance of Stefan flow – first derived and described in the 19th century – is certain. Indeed, engineers
57 necessarily account for its role in heat and mass transfer (Abramzon and Sirignano, 1989) when precisely
58 controlling industrial processes that include phase change, such as combustion. For these reasons, it is to
59 be expected that a more accurate means of estimating $w|_0$ for the atmospheric boundary layer can be
60 achieved by rigorous examination of known surface flux densities in 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 momentum 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 velocity and density of air, respectively, while w_i and ρ_i are the those
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 $w \neq 0$), 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 those of its components (Kowalski, 2012), where the weighting
91 factors 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
$$F_{i,M} = -\rho k \frac{\partial f_i}{\partial z}, \quad (2)$$

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). Considering only flow within the tube (at point 1), whether
140 laminar or turbulent, it clearly realizes non-diffusive transport of salt, since the salt has no particular
141 behaviour with respect to the fluid, but simply goes with the flow. There are no scalar gradients within the
142 tube, and so there is neither diffusion nor advection. Let us now describe diffusive transport processes
143 within the pool (at point 2), and the nature (whether absolute or relative) of the relevant fluid properties
144 whose gradients determine them by defining sources/sinks, using two illustrative case scenarios.

145



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

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

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

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

180
181 2) *Let us now specify that the water in the pool has the same (freshwater) salinity as that coming from*
182 *the tube ($35 \cdot 10^{-5}$). If we furthermore remove both surface evaporation and heating from scenario (1),*
183 *then the temperature remains constant and the salinity corresponds uniformly to that of freshwater,*
184 *but the pool accumulates mass. In this case, there are convergences in the non-diffusive transports of*
185 *water, salt, and heat content: fluxes into the pool are positive, while fluxes out are null. However,*



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

195 **2.3 An advection-diffusion synopsis**

196 The analyses that follow rely on the succeeding key points drawn from sections 2.1 and 2.2. Advection
197 and diffusion depend on gradients in scalars whose nature is relative rather than absolute. In
198 incompressible thermodynamics, the relevant gradients are those in the temperature, and not the heat
199 content. For trace constituents, the relevant scalar is the mass fraction (e.g., salinity) and not the species
200 density. Advection and diffusion are otherwise physically very distinct. Like non-diffusive transport,
201 diffusion is a vector whose vertical component is of particular interest in the context of surface-
202 atmosphere exchange. By contrast, advection is a scalar; for some arbitrary quantity ξ , it is defined as the
203 negative of the inner product $\mathbf{v} \cdot \nabla \xi$, where \mathbf{v} is the fluid velocity and ∇ is the gradient operator. To be
204 clear, it can make sense to speak of “upward diffusion”, but certainly not “upward advection”. The
205 tendency, in the science of surface-atmosphere exchange, to speak of “vertical advection” (e.g., Rannik et
206 al., 2009) is intimately related to an assumption of horizontal homogeneity, precluding horizontal scalar
207 gradients particularly in the direction of the mean wind.
208

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



222 3 Analysis

223 3.1 Framework

224 The analysis will focus on a system defined as a mixture of gas molecules of different species, whose
225 momentum will be examined. The system's mass is defined (Table 2) by gas components in a ratio that
226 corresponds quite closely to that of the atmosphere (Wallace and Hobbs, 2006) but updated to more
227 closely reflect actual atmospheric composition. At a representative ambient temperature ($T = 298$ K) and
228 pressure ($p = 101325$ Pa), the many millions of molecules forming this system occupy a volume of 10^{-15}
229 m^3 with 70% relative humidity. The system geometry will be specified in four different ways, according
230 to the different spatial scales for which $w|_0$ is to be described:

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

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

251

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

259



260 3.2 The vertical velocity at the surface boundary

261 Knowledge regarding surface exchange (gas flux densities) has advanced to the point where the boundary
262 condition for the vertical velocity ($w|_0$) can be estimated from conservation of linear momentum –
263 applying Eq. (1) to the system defined in Table 2 –, and vastly simplified to a simple function of the
264 evaporation rate (E). The species flux densities ($w_i\rho_i$) within the system represent the surface exchanges
265 of the corresponding gas species (i). Scale analysis of surface gas exchange magnitudes, published from
266 investigations at a particularly well-equipped forest site in Finland (Table 3), reveals that for the water
267 vapour species ($i=4$), the flux density ($E = w_4\rho_4$) is orders of magnitude larger than both the flux density
268 of any dry air component species and even the net flux density of dry air. Such dominance by water
269 vapour exchanges is representative of most surfaces worldwide. This is especially so because the two
270 largest dry air component fluxes are opposed, with photosynthetic/respiratory CO_2 uptake/emission
271 largely offset by O_2 emission/uptake (Gu, 2013). Hence, following tradition in micrometeorology (Webb
272 et al., 1980), dry air exchange can be neglected, allowing the elimination from Eq. (1), when applied at
273 the surface, of all species flux densities except for that of water vapour (H_2O ; $i=4$). Therefore, net air
274 transfer across the surface can be approximated very accurately as

$$275 \quad w|_0 \rho|_0 = w_4|_0 \rho_4|_0 = E, \quad (3)$$

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

$$280 \quad w|_0 = \frac{E}{\rho_4|_0}. \quad (4)$$

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

293
294 Given that the surface boundary is static, it may well be asked why there is a non-zero boundary condition
295 for the vertical velocity of air. The answer is that evaporation induces a pressure gradient force that
296 pushes air away from the surface. Evaporation into air increments the water vapour pressure and thereby



297 the total pressure, according to Dalton's law. If evaporation were to proceed until achieving equilibrium,
298 the pressure added by evaporation would correspond to the saturation vapour pressure (e_s ; Figure 2),
299 whose temperature dependency has been quantified empirically and is described by the Clausius-
300 Clapeyron relation. It is this evaporation-induced pressure gradient force that pushes the manometer in
301 Fig. 2 to its new position, and similarly that drives winds away from the surface.

302

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

317
$$w = \frac{E}{\rho} . \tag{5}$$

318

319 3.3 Mechanisms of gas transport at the surface

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

331

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

333
$$F_{i,non} = w\rho_i , \tag{6}$$



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

$$335 \quad F_{i,non} = E f_i, \quad (7)$$

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

340

341 Interpreting decomposed transport is simplest when examining a gas whose surface exchange is very well
342 known, such as the null value for inert Argon (Ar) that constitutes ca. 1.3% of dry atmospheric mass
343 (Wallace and Hobbs, 2006). Considering the state variables defined by Table 2 and the evaporation rate
344 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-
345 diffusive Ar transport ($F_{3,non}$). To comprehend this, it helps to recall that the constant addition of H_2O
346 dilutes dry air at the surface and promotes its downward diffusion. For a null net flux of inert Ar to exist,
347 downward diffusion of this dry air component must exactly cancel the upward non-diffusive transport,
348 and therefore is $458 \mu\text{g m}^{-2} \text{s}^{-1}$ for the state and evaporative conditions specified above. These opposing
349 non-diffusive and diffusive Ar transport processes are quite analogous to case scenario 1 of Section 2.2, at
350 the instant t_f when the fluid emitted into the pool has a diluting effect. Such dual transport mechanisms
351 are also relevant for vital gases, with different transport directions and degrees of relevance, depending on
352 the density and flux density of the gas in question.

353

354 For H_2O , the two types of gas transport mechanisms operate in tandem, with the non-diffusive component
355 contributing a fraction of upward H_2O transport that, according to Eq. (7), is exactly the water vapour
356 mass fraction or specific humidity (Wallace and Hobbs, 2006)

$$357 \quad q \equiv f_4 \equiv \frac{\rho_4}{\rho}. \quad (8)$$

358 This is just 2% for the state conditions previously specified, but can approach 5% for very warm
359 evaporating surfaces and/or high-altitude environments. The breakdown of H_2O transport into diffusive
360 and non-diffusive components is analogous to case scenario 1 of Section 2.2 at an instant prior to t_{eq} when
361 the fluid introduced to the pool is highly concentrated, in comparison with the fluid already in the pool. In
362 any case, non-diffusive H_2O transport is generally secondary to diffusive transport, but its neglect in an
363 ecophysiological context can lead to larger relative errors, as will be shown in Section 4.

364

365 For CO_2 , which usually migrates downward during evaporative conditions because of photosynthetic
366 uptake, upward transport of a non-diffusive nature is even more relevant, opposing the downward flux
367 due to diffusion. To see this, let us examine the typical gas transport magnitudes of Table 2 and the
368 atmospheric state conditions specified above. According to Eq. (7), non-diffusive CO_2 transport ($F_{5,non}$) is
369 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
370 downward CO_2 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
371 accounting for the non-diffusive resistance to net transport, the CO_2 diffusivity would be underestimated



372 by ca. 20%. The case of CO₂ uptake is not analogous to any pool/tube scenario in Figure 1. However,
373 different conditions with equal evaporation ($E = 36 \text{ mg m}^{-2} \text{ s}^{-1}$) and CO₂ emission in the amount of 21.5
374 $\mu\text{g m}^{-2} \text{ s}^{-1}$ (by respiration, for example) would correspond to the case of zero CO₂ diffusion (as at the
375 instant t_{eq}), since the CO₂ mass fractions of both the atmosphere and the gas mixture emitted by the
376 surface are identical. Viewed in the traditional diffusion-only paradigm, such a situation involving a net
377 flux but no gradient ($F_3 = F_{3,\text{non}}$) would require a physically absurd infinite diffusivity. At this same
378 evaporation rate, but with lower CO₂ emission, diffusion of CO₂ would be downward, towards the surface
379 which is a source of CO₂ but a sink of the CO₂ mass fraction (analogous to salinity in case scenario 1 of
380 Section 2.2 at some instant between t_{eq} and t_f when the fluid emitted to the pool has a diluting effect).
381 Whatever the direction of net CO₂ transport, these case examples demonstrate the need for sometimes
382 substantial rectifications to flux-gradient relationships – whether expressed as a conductance, resistance,
383 deposition velocity, or eddy diffusivity (K-theory), – when correctly accounting for non-diffusive
384 transport.

385 4 Discussion

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

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 $31 \mu\text{m s}^{-1}$ 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. $6 \mu\text{m}$) 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 CO₂ ingress – has been
410 previously conceived, but broadly neglected in the field of ecophysiology.

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 among plant physiologists (von Caemmerer and Farquhar,
418 1981). Similarly, Leuning (1983) recognized the relevance of non-diffusive transport and furthermore
419 identified excess pressure inside the stomatal cavity as the impetus for the outward airstream (which he
420 termed “viscous flow”), but had little impact on the mainstream characterization of stomatal conductance.
421 Rather, important aspects of ecophysiology continue to hinge upon the assumption that diffusion alone
422 transports vital gases through plant pores, disregarding both the above-mentioned studies and more
423 importantly the fact that gas transport mechanisms through such apertures were accurately described by
424 one of the great physicists of 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. The phenomenon
437 of transpiration through a stoma is a reasonable proxy for a Stefan tube, the main difference being that
438 evaporation in the Stefan tube depletes the pool of evaporating liquid, whose surface therefore recedes
439 downward. By contrast, the evaporating water in the stomatal cavity is continually replenished by
440 vascular flow from within the plant; if anything, this reinforces the magnitude of the upward vertical air
441 velocity, in comparison with the Stefan tube, consistent with that derived from momentum conservation
442 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 boundary condition for the vertical velocity is $w|_0 = \frac{E}{\rho|_0}$, where $\rho|_0$ is the air density
480 at the surface. This non-zero vertical velocity describes Stefan flow and implies gas exchange of a non-
481 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



486 **Acknowledgements**

487 This work is dedicated, with fondness and great esteem, to the memory of Ray Leuning whose insights
488 led to substantive improvements both in this work and broadly in the science of surface gas exchanges.
489 Investigation into this matter was funded by Spanish national project GEISpain (CGL2014-52838-C2-1-
490 R). The author thanks P. Serrano-Ortiz, E. P. Sánchez-Cañete, O. Pérez-Priego, S. Chamizo, A. López-
491 Ballesteros, R.L. Scott, J. Pérez-Quezada and anonymous reviewers for bibliographical guidance,
492 comments and criticisms that helped to clarify the manuscript.
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495 **References**

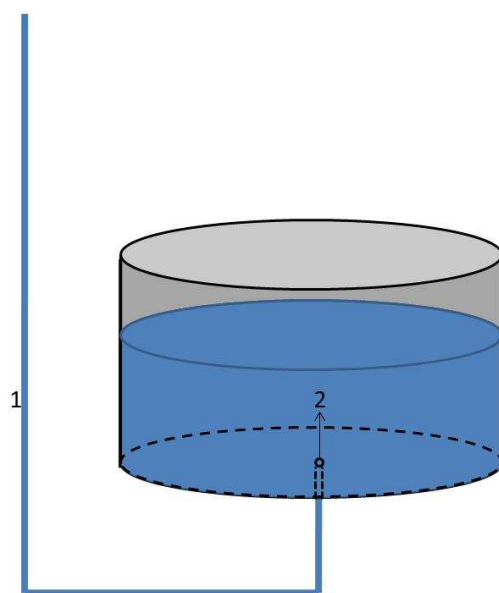
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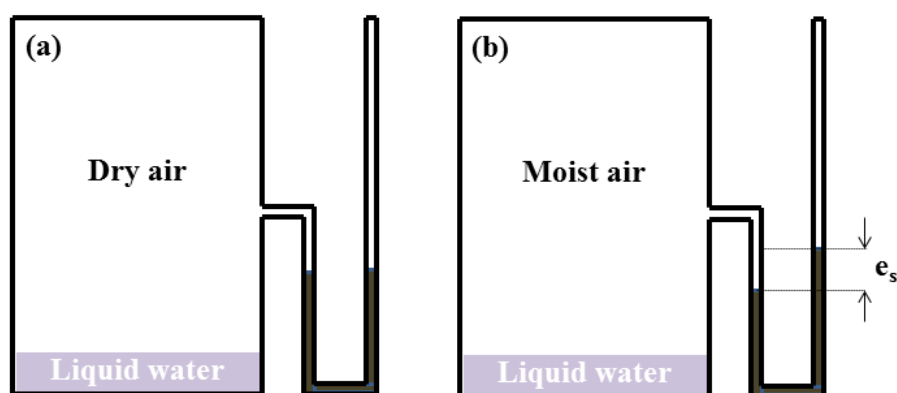


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Figure 1: A pool of water being fed from below by a tube. The points indicate water (1) in the tube, and (2) in the pool. The arrow indicates the direction of flow.



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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.



590 **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 ζ	0 (scalar)
ξ_i	The magnitude of arbitrary variable ζ for gas species i	Depends on ζ	0 (scalar)
$\nabla\xi$	The spatial gradient in arbitrary variable ζ	Depends on ζ	1 (vector)
$[\xi]_0$	The lower boundary condition for arbitrary variable ζ	Depends on ζ	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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593 **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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596 **Table 3: The first six air components by their surface exchange scale magnitude, and the net exchange of air as**
597 **the sum of these flux densities. Representative surface exchanges are taken from the Finnish boreal forest site**
598 **(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	0.0000088	0.0000002	(Aaltonen et al., 2011)	7
Air	35.98	-	This study	-

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600