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Revisiting the thermodynamic derivation of the Penman-Monteith Equation

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Abstract. The Penman-Monteith (PM) equation is the most commonly used method for determining latent heat fluxes (λE) from vegetated land surfaces and is regarded as a best practice for calculating evapotranspiration. It is based on a general energy balance approach, in which evaporation is derived indirectly by approximating the sensible heat flux (SH). The temperature difference between the surface and the near-surface air, which drives SH and is required to compute the heat flux, is eliminated from the associated system of equations by introducing the slope of the saturation vapor pressure curve at the air temperature (s_{Ta}). However, in the PM equation this slope does not describe, in the original sense, a change in the thermodynamic state of a system; rather, it represents the ratio of a spatial heat and a constructed moisture potential difference between the surface and the near-surface air. In the thermodynamic derivation of the PM equation by Monteith (1965), this apparent physical inaccuracy is resolved by describing the evaporation process not anymore through classical flux-gradient relationships but through the thermodynamic state change of the near-surface air. This derivation, however, is based on the assumption that the sensible heat flux from the surface heats the air mass into which evaporation occurs. This heat input increases the saturation vapor pressure of the near-surface air, allowing the partitioning of SH and λE according to s_{Ta}. For vegetated surfaces this assumption does not hold, because the phase transition during transpiration occurs into the air inside the leaf and not into the air close to the surface, into which the sensible heat flux takes place. For the air inside a leaf, however, the sensible heat flux into the atmosphere does not constitute an energy input but rather an energy sink; therefore Monteith's (1965) thermodynamic concept cannot be transferred to vegetated surfaces. Thus, the use of s_{Ta} to partition the available energy at the surface can only be physically justified for water saturated, unvegetated surfaces and the PM equation should therefore be applied only under such conditions.

1 Introduction

Evaporation (E) is a fundamental process in the Earth system. The radiation absorbed at the Earth's surface heats the water molecules, causing them to transition into the gas phase more frequently. The energy required for this phase transition, λ ($\approx 2\,500$ J g^{-1}), is therefore removed from the surface and transferred to the atmosphere. Consequently, evaporation plays a crucial role in the Earth's energy balance by linking the surface and the atmosphere (Seneviratne et al., 2010). An accurate representation of E is thus a prerequisite for successful weather and climate modeling.

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From a physical point of view, the evaporation process is governed by the kinetic-energy level of the water molecules. In the liquid phase the kinetic energy of the molecules is lower than in the gas phase; molecular motion is therefore less pronounced, and the average distance between molecules is relatively small. The intermolecular bonds, arising from the dipole moment of the water molecules, are consequently strong.

According to the Maxwell-Boltzmann distribution, water molecules at a given temperature do not all move at the same speed: some move faster, others slower. Molecules with higher velocities increase the distance to their neighbours through their motion, thereby weakening the attractive forces between them. A subset of these fast molecules possesses enough kinetic energy to perform the work that is necessary to overcome the intermolecular attractions and escape into the gas phase. Hence, the higher the kinetic-energy level of the liquid water, the larger the fraction of molecules that have sufficient speed to transition to the gas phase. Or in other words, higher water temperatures lead to a higher evaporation rate.

However, an increased evaporation rate also means that more water molecules accumulate in the air. This increases the likelihood that water vapor molecules will come again into contact with the surface and be recaptured. When the water vapor concentration in the air becomes so high that, statistically, the number of molecules condensing back onto the surface equals the number evaporating at a given temperature, the air is saturated with water vapor. In this saturated state, the number of phase transitions in both directions is equal and net evaporation is zero (see Figure 1). If the water vapor concentration is below saturation, net evaporation into the near-surface air occurs; if it is higher, a net condensation takes place.

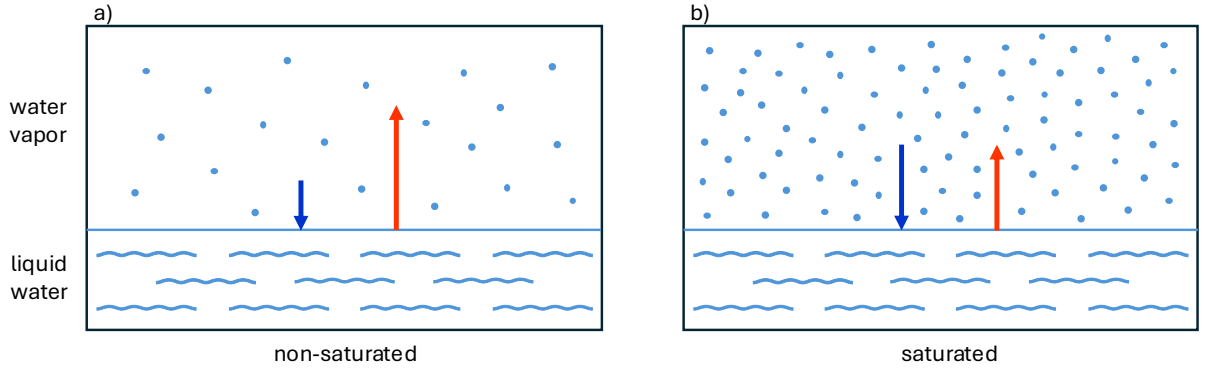

Figure 1: Schematic of the water vapor fluxes between a water surface and the atmosphere for a) non-saturated, and b) saturated air conditions. The red arrow indicates the vaporization of water molecules, and the blue arrow indicates their condensation. The figure is adapted from Liljequist & Cehak, (2013).

These molecular phase transitions take place directly at the interface between the water surface and the lowest millimeters of the atmosphere. As this interface is very small, a thermodynamic equilibrium is quickly established, so that saturated conditions can be assumed. The interface is in turn in contact with the air layers above it, which are not saturated. This means that between both a water potential difference evolves which triggers a diffusive flux. Diffusion describes a statistical net flux, which is

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caused by the undirected motion of the molecules based on their internal kinetic energy (Atkins & de Paula, 2002). From a point of a high water vapor concentration (in this case the air closest to the water surface e_s (in Pa), statistically more water vapor molecules diffuse into an area of lower concentrations (air above e_a (in Pa)) than vice versa.

This net diffusive flux therefore transports water vapor from the contact area with the water surface into the air layers above, which reduces the water vapor concentration close to the water surface. This in turn disturbs the thermodynamic equilibrium that had been established in the interface so that this air becomes undersaturated. As a result, a net evaporation starts. In other words, the water concentration difference that triggers the diffusive flux drives the phase transition. In order to reach again a thermodynamic equilibrium in the interface, evaporation increases by the amount of the diffusive flux.

Evaporation can therefore be described as a transport of latent heat λE (in W m^{-2}) that is driven by the moisture-potential difference between the saturated (air close to the) surface e_s and the unsaturated air e_a:

$$\lambda E = c_{\lambda E}(e_s - e_a) \tag{1}$$

Equation (1) represents, in the classical physical sense, a flux-gradient relationship that is scaled by a transfer coefficient $c_{\lambda E}$ (in m s^{-1}). The parameter $c_{\lambda E}$ is a proportionality factor that describes the extent to which the turbulent flux of latent heat is modified by atmospheric processes. Consequently, solving Eq. (1) requires knowledge not only of the moisture-potential difference but also of the transfer coefficient. In practice, this information is usually not available. For this reason, a variety of methods have been developed over the years to approximate the evaporation process empirically. The most common approaches have generally tried to establish an empirical relationship between the potential evaporation and the influencing factors of solar radiation and air temperature (e.g., Thornthwaite 1948; Blaney & Criddle 1950; Turc 1961). In a method that is widely used in Central Europe, Haude (1954) employed the vapor pressure deficit to estimate potential evaporation.

An indirect way to quantify evaporation is the Bowen-Ratio method (e.g., Brutsaert 1982). Rather than approximating evaporation directly through empirical relationships, this technique derives evaporation indirectly from the surface energy balance:

$$R_n - G = SH + \lambda E \tag{2}$$

R_n denotes the net radiation (in W m^{-2}), G the ground heat flux (in W m^{-2}), and SH the sensible heat flux (in W m^{-2}). Analogously to Eq. (1), SH can be expressed as a transport of sensible heat that is driven by the temperature difference between the surface T_s and the near-surface air T_a (in K) and scaled by a transfer coefficient c_{SH} (in m s^{-1}).

$$SH = c_{SH}(T_s - T_a) \tag{3}$$

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To use the Bowen-Ratio Method, one must first know how much energy is available at the surface and, second, the relationship between λE and SH. One way to express this relationship is the Bowen Ratio β:

$$\beta = \frac{SH}{\lambda E} = \frac{c_{SH}(T_s - T_a)}{c_{\lambda E}(e_s - e_a)} \quad (4)$$

Since both sensible and latent heat transport occur through turbulent eddies and therefore rely on the same physical processes, the Bowen-Ratio method assumes that the two transport mechanisms are fundamentally similar and that the transfer coefficient c_{SH} can be set equal to $c_{\lambda E}$. That means that only the potential differences need to be linked. However, the required information on the surface conditions (T_s, e_s) is difficult to measure and therefore generally cannot be used to calculate the Bowen ratio. Penman (1948), however, developed an approach that allows to approximate these potential differences by atmospheric state variables. Monteith (1965) provided a thermodynamic derivation of this method and extended its applicability to vegetated surfaces. The resulting Penman-Monteith (PM) equation (Monteith, 1965) is today probably the most widely used method for determining latent heat fluxes from vegetated land surfaces and is regarded as the gold standard for calculating evapotranspiration (e.g., Allen, 1986).

2 The Derivation of the Classic Penman Equation

The original form of the equation was derived by Penman (1948) for the evaporation of open water surfaces and saturated soils. The problem of the missing information on the potential differences between the surface and the atmosphere in Eqs. (1) – (3) was addressed by Penman (1948) through the introduction of an additional term that links the spatial temperature difference between T_s and T_a to a moisture-potential of saturated air. To do this, he related the difference between the saturation humidities at the surface e_s and the near-surface air e_d (calculated from the Clausius–Clapeyron equation for T_a) to $T_s - T_a$ and approximated this hypothetical ratio with the slope s_{Ta} of the saturation vapor pressure (in Pa K^{-1}) curve at T_a:

$$s_{T_a} = \frac{e_s - e_d}{T_s - T_a} \quad (5)$$

This linearized form of the slope s of the saturated vapor pressure curve at T_a has been questioned quite extensively in the literature (e.g., Paw & Gao, 1988; McArthur, 1990; Milly, 1991), but it is accepted for the subsequent derivation.
Substituting Eq. (3) into Eq. (2) and replacing the temperature difference $T_s - T_a$ with the relationship given in Eq. (5) yields

$$R_n - G = \lambda E + \frac{c_{SH}}{s_{Ta}}(e_s - e_d) \quad (6)$$

where $e_s - e_d$ can be expressed by expansion as follows:

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$$e_s - e_d = (e_s - e_a) - (e_d - e_a) \tag{7}$$

If, in this equation, the spatial moisture-potential difference $e_s - e_a$ is replaced by the ratio given in Eq. (1) and this substitution is inserted into Eq. (6), the following result is obtained:

$$R_n - G = \lambda E + \frac{c_{SH}}{s_{Ta}}(e_d - e_a) - \frac{c_{SH}}{c_{\lambda E} s_{Ta}} \lambda E \tag{8}$$

In contrast to the Bowen-Ratio method, Penman (1948) does not assume that the transfer coefficients c_{SH} und $c_{\lambda E}$ are equal. Although sensible and latent heat are both transported in the near-surface air by turbulent eddies, and therefore rely on the same underlying physical processes, their transport behavior within the eddies is not identical. This discrepancy arises because the transport media for sensible and latent energy, dry air on the one side and water vapor on the other, have different inertia. The difference in inertia results from differences in the molar masses between water vapor and dry air. The ratio of the molar mass of water vapor to that of dry air (μ) is incorporated into the psychrometric constant γ (in Pa K^{-1}):

$$\gamma = \frac{p_a c_{pa}}{\lambda \mu} \tag{9}$$

p_a is the atmospheric pressure (in Pa) and c_{pa} the heat capacity of the air (in J kg^{-1} K^{-1}). Through the consideration of p_a and c_{pa} in the psychrometric constant, the ratio of the transfer coefficients c_{SH} and $c_{\lambda E}$ can therefore be approximated by γ:

$$\gamma = \frac{c_{SH}}{c_{\lambda E}} \tag{10}$$

The ratio of the transfer coefficients c_{SH} and $c_{\lambda E}$ in Eq. (8) can now be expressed by γ as given in Eq. (10). To account for the effect of varying wind speeds on the exchange processes, Penman (1948) introduced an additional wind function f_w, which was derived empirically from observations. This wind function replaces the remaining atmospheric transfer coefficient c_{SH} in the equation. After a series of rearrangements, the Penman equation is finally obtained:

$$\lambda E = \frac{s_{Ta} * (R - G) + \gamma * f_w (e_d - e_a)}{s_{Ta} + \gamma} \tag{11}$$

As Eqs. (6) and (8) demonstrate, Penman (1948) essentially approximates the sensible heat flux and combines it with the available energy at the surface $R_n - G$, leaving λE as the residual term derived from the energy balance.

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3 The Thermodynamic Derivation of the Penman-Monteith Equation

The introduction of s_{Ta} in Eq. (5) was, first and foremost, a mathematically clever move to eliminate the temperature difference $T_s - T_a$ from the energy balance and approximate it with atmospheric variables that can be obtained from routine measurements at weather stations. Conceptually, however, the use of s_{Ta} raises several questions. s_{Ta} initially describes how the thermodynamic state of a system of saturated air changes when energy is added, i.e., how the system's heat and moisture content evolve. In contrast, $T_s - T_a$ does not represent a temperature change of a single system, it is a spatial potential difference. Thus, by introducing s_{Ta}, a spatial potential difference that drives the transport of sensible heat is related to a moisture potential of saturated air. However, this moisture potential between the water-saturated surface and the saturation humidity at air temperature has, strictly speaking, nothing to do with the latent flux, when λE is expressed through a classic flux-gradient relationship. In such an approach, as used by Penman (1948), λE is driven by the moisture potential between the saturated surface and the actual moisture content in the air (Eq. 1), and this moisture content is independent of temperature. The saturation humidity at the air temperature and the associated vapor pressure deficit play a role only in thermodynamic considerations (see Figure 1). Through s_{Ta}, Penman (1948) therefore links a constructed spatial moisture potential between the surface and the air with a spatial temperature potential difference. In other words, the potentials of two spatially separated systems are connected by a thermodynamic state change of a single system. A step that, of course, can be questioned from a physical standpoint.

Monteith (1965) provided an explanation for why the introduction of s_{Ta} can also be justified from a thermodynamic perspective to describe λE. Rather than explaining the evaporation process in terms of a flux-gradient relationship through spatial potential differences, he describes it in terms of the thermodynamic state change of the near-surface air into which evaporation occurs. In this view, the total evaporation rate of a wet surface, E_G (in kg m^{-2} s^{-1}), is expressed as the sum of an adiabatic component E_1 and a diabatic component E_2.

$$E_G = E_1 + E_2 \tag{12}$$

For the description of the adiabatic component of evaporation E_1, the air mass into which evaporation takes place and its contact with the surface are initially defined as a closed, adiabatic system that exchanges no energy with the surrounding environment. That means that any change in the internal energy state of the system, e.g., a change in its latent heat $\delta\lambda E_1$, is always accompanied by a corresponding change in the sensible heat δSH_{ad} of the system (equal magnitude but opposite sign). Thus, the following applies:

$$\delta\lambda E_1 + \delta SH_{ad} = 0 \tag{13}$$

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If the air mass is undersaturated, a net evaporation from the surface into the air continues until saturation is reached and the air and the surface attain a thermodynamic equilibrium. However, energy is required for this evaporation from the surface. Since the system is treated as closed and no external energy sources exist, the energy needed for the additional phase transition must be provided from the system itself. The air supplies this energy in the form of sensible heat. The surface takes this sensible heat, which raises the kinetic-energy level of the water molecules, causing them to transition into the gas phase more frequently. As a result, the latent heat content of the air increases. In other words, the air transports energy in the form of sensible heat to the surface and, in return, receives an equal amount of energy as latent heat (Eq. 13). Thus, the air cools while simultaneously becoming more humid. The relationship between a temperature decrease ΔT_1 and the adiabatic evaporation rate up to saturation E_1 can be expressed by the psychrometer equation:

$$E_1 = \gamma(\Delta T_1) \tag{14}$$

When the energetic state of an air parcel is plotted on a temperature/water vapor pressure diagram (Figure 2), P_0 denotes the initial undersaturated state and the black line represents the saturation vapor pressure curve. The more sensible heat the air transfers to the surface, i.e., the greater the cooling of the air is, the higher the water-vapor pressure rises. In this context, γ characterizes the slope of this moisture increase. At the point where the line with the slope γ intersects the saturation vapor pressure curve (P_1), a new thermodynamic equilibrium is reached and no further evaporation occurs. The evaporation rate E_1 therefore constitutes the adiabatic component of the total evaporation rate E_G.

Moreover, the reasoning behind Eq. (13) for a closed adiabatic system implies that λE_1 must have the same magnitude as the adiabatic sensible heat flux and can therefore also be calculated using SH_{ad}:

$$SH_{ad1} = \frac{\rho_a c_{pa} \Delta T_1}{r_a} = \lambda E_1 \tag{15}$$

where ΔT_1 is the difference between the initial air temperature T_{P0} and the wet-bulb temperature T_{P1} that is attained once saturation is reached, that is, the temperature reduction of the air caused by the adiabatic sensible heat flux toward the surface. ρ_a is the air density (in kg m³) and r_a denotes the aerodynamic resistance of the air (in s m^{-1}), or, equivalently, the rate at which a given air volume is transported per unit area. Analogous to Eqs. (1) and (3), a resistance coefficient can be regarded as the reciprocal of a transfer coefficient and can thus replace it. Equation (15) therefore represents the adiabatic component of the total evaporation as described by Slatyer & McIlroy (1961).

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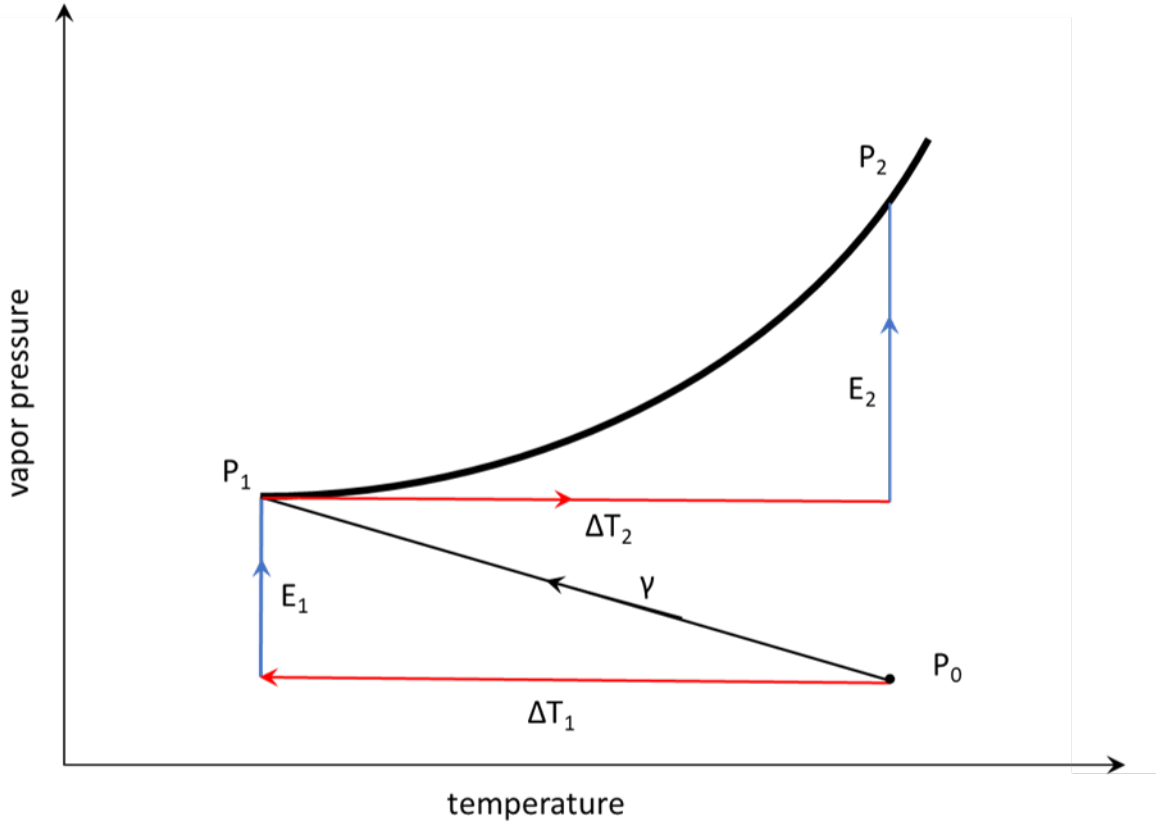

Figure 2: Temperature/water vapor pressure diagram for the evaporation of water and saturated soil surfaces

Under these equilibrium conditions, further evaporation into an already saturated air mass can occur only if the temperature of that air mass rises, thereby increasing its capacity to hold water vapor. Consequently, an external amount of energy Q must be supplied to the system to enable additional diabatic evaporation E_2. In this process, the sun provides the surface with energy in the form of electromagnetic radiation. The surface warms as a result and transfers sensible heat to the adjacent air mass. This warming of the air mass, in turn, raises the saturation vapor pressure and thus creates undersaturation, inducing further evaporation until a new equilibrium state (P_2) is reached (in Figure 2 the temperatures T_{P0} und T_{P2} are shown as identical, although this need not be the case for the derivation of the diabatic component). The energy Q released by the surface therefore raises the temperature by ΔT_2, and the evaporation rate increases by E_2. Thus, the energetic state of the air increases diabatically through the sensible heat flux SH_{di} and the latent energy input λE_2:

$$Q = SH_{di} + \lambda E_2 \tag{16}$$

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The extent to which the evaporation rate E_2 in the saturated air increases as a result of a temperature rise ΔT_2 can be approximated by a linearized form of the slope s of the saturation vapor pressure curve between P_1 and P_2:

$$E_2 = s(\Delta T_2) \tag{17}$$

From Eq. (16) it follows that the diabatic sensible heat flux SH_{di} can also be expressed as the difference between Q and λE_2. If now Eq. (17) is not anymore defined in terms of changes in water vapor content and temperature, as described, for example, in Zerihun et al. (2023), but in terms of latent and sensible energy states, and SH_{di} is replaced with the difference $Q - \lambda E_2$, then simple rearrangements yield the diabatic component of total evaporation:

$$\lambda E_2 = \frac{sQ}{s+\gamma} \tag{18}$$

To derive the Penman-Monteith equation from the adiabatic component (Eq. 15) and the diabatic component (Eq. 18) of the total evaporation, it is further assumed that T_{P0} and T_{P2} are identical. It follows that:

$$\Delta T_1 = \Delta T_2 \tag{19}$$

If we now substitute Eq. (14) and Eq. (17) into Eq. (12), taking Eq. (19) into account, we obtain

$$E_G = \Delta T(s + \gamma) \tag{20}$$

When solved for ΔT, this yields:

$$\Delta T = \frac{E_G}{(s+\gamma)} \tag{21}$$

Taking Eq. (19) into account, ΔT_1 in Eq. (15) can now be replaced by ΔT from Eq. (21) to calculate the adiabatic latent heat flux λE_1:

$$\lambda E_1 = \frac{\rho_a c_{pa}(e_{P2} - e_{P0})/r_a}{s+\gamma} \tag{22}$$

Equation (22) represents the first, the adiabatic component of the Penman-Monteith equation, where the term $(e_{P2} - e_{P0})$ corresponds to the difference $(e_d - e_a)$ in Eq. (11), i.e., the achieved saturation humidity minus the initial specific humidity of

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the air into which evaporation occurs. The wind function f_w, which in the original Penman formulation accounts for the effect of wind speed on the atmospheric transport and therefore serves as a transfer coefficient, is replaced in the thermodynamic derivation of Monteith (1965) by the introduction of the aerodynamic resistance coefficient r_a.

If Eq. (22) is combined with the diabatic component of evaporation from Eq. (18), the resulting expression provides the equation for the calculation of the total latent heat flux of a saturated surface as formulated by Monteith (1965):

$$\lambda E_G = \frac{s(R_n - G)}{s+\gamma} + \frac{\rho_a c_{pa}(e_d - e_a)/r_a}{s+\gamma} \tag{23}$$

The external energy input Q into the air mass into which evaporation occurs corresponds to the sum of sensible heat (SH) and latent heat (λE) released by the surface and can be expressed, according to Eq. (2), as $R_n - G$.

Furthermore, Monteith (1965) extended the applicability of the PM equation to vegetated surfaces in his thermodynamic derivation. He recognized that, for vegetated areas, the stomatal resistance r_s must be taken into account in addition to the aerodynamic resistance r_a. For this purpose, he modified the psychrometric constant γ in Eq. (23), which in the PM equation is used as the ratio of the transfer coefficients for sensible and latent heat, by incorporating the stomatal resistance r_s as follows:

$$\gamma^* = \gamma * \left(1 + \frac{r_s}{r_a}\right) \tag{24}$$

4 A Critical Discussion of the Consistency of the Thermodynamic Derivation of the Penman-Monteith Equation

In his thermodynamic derivation, Monteith (1965) describes evaporation as the sum of two thermodynamic sub-processes: an adiabatic evaporation that is driven by the initial undersaturation of the air, and a diabatic evaporation that, through an external supply of sensible heat to this adjacent air mass, raises the saturation vapor pressure and thereby induces additional evaporation. This derivation, now known as the Penman-Monteith equation for calculating evaporation from saturated surfaces, is more complex than the classic formulation of Penman (1948), but it opens new perspectives on the PM equation and provides opportunities to interpret it physically and thus to understand it better (Zerihun et al., 2023).

For instance, via this alternative derivation, Monteith (1965) was able to show that the use of the slope of the saturation vapor pressure curve s_{Ta} to approximate the spatial temperature difference can also be justified from a thermodynamic point of view. In his process-based derivation the evaporation process is no longer described in terms of potential differences between the surface and the atmosphere, but solely in terms of the thermodynamic state change of the air mass into which evaporation occurs. In doing so he replaced the spatial temperature difference $T_s - T_a$, for which Penman (1948) introduced s_{Ta}, by the wet-bulb temperature change ΔT_I, i.e., the change in heat of a cooling system. In this way, the physical inconsistency is resolved that arises when a spatial temperature difference is approximated by a constructed thermodynamic state change of a system whose moisture change is not caused by the system's own temperature change, but by the hypothetical potential difference of

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saturated air for the spatial temperature difference $T_s - T_a$. Thus, in Penman's original derivation s_{Ta} is not used to describe a thermodynamic state change but to approximate the ratio of spatial potential differences.

From a purely mathematical perspective, s_{Ta} is initially employed in the PM equation to partition the available energy at the surface, $R_n - G$. In other words, $R_n - G$ is divided in accordance with the change of the ratio between the sensible and latent energy contents of a system that occurs when the air's saturation vapor pressure increases due to a rise in temperature. However, according to the thermodynamic derivation, the total evaporation amount E_G is larger than that obtained by this diabatic partitioning of $R_n - G$, because the adiabatic component of evaporation must also be considered. As a result, the total evaporation continues to increase, which reduces the portion of sensible heat in $R_n - G$ that is partitioned by s_{Ta}. Referring to the graphical illustration of evaporation in Figure 2, this means that the adiabatic cooling of the air mass caused by the adiabatic evaporation therefore has to be first compensated by the sensible heat flux. Only when T_{P2} exceeds T_{P0}, a net transport of sensible heat from the surface to the adjacent air occurs.

However, a critical step in the thermodynamic derivation of the Penman-Monteith equation is the simplifying assumption that $T_{P2} = T_{P0}$ (Eq. 19). Only for this case Eqs. (20) and (21) are valid and can subsequently be substituted into Eq. (22). Therefore, the thermodynamic derivation of the PM equation describes a special case of evaporation in which the available energy ($R_n - G$) is conceptually converted solely into the release of latent heat into the air, while the net sensible heat flux SH_G is zero. Conversely, this does not apply to the latent heat fluxes that are actually calculated using the PM equation. For instance, the adiabatic evaporation component is small when moisture differences between the saturated surface and the undersaturated air are low; accordingly, the reduction in the diabatically partitioned sensible heat flux is small, and $SH_G > 0$. Strictly speaking, the mathematical relationships employed in the PM equation for these calculations are only applicable to the case where $T_{P2} = T_{P0}$ and can therefore only yield physically consistent results for that specific condition.

However, such a steady state where $T_{P2} = T_{P0}$ can indeed be assumed for evaporation processes from vegetated surfaces, provided that one assumes that a leaf temperature is always established at which the leaf's energy balance is in equilibrium. But in the case of plant transpiration, this does not imply that ($R_n - G$) is entirely converted into a latent heat flux, as it would theoretically follow from Monteith's (1965) original thermodynamic derivation. In this thermodynamic concept, the calculation of the diabatic evaporation component λE_2 rests on the assumption that surface warming leads to a sensible heat flux (SH_{di}) into the adjacent air mass into which evaporation occurs. This supply of sensible heat increases the capacity of the air mass to hold water vapor, thereby inducing additional evaporation. The sum of these sensible and latent heat fluxes into the adjacent air mass constitutes the energy input Q (Eq. 16). Thus, the sensible heat flux from the surface SH_{di} acts as an energy input for the air layer into which the phase transition takes place.

During the transpiration process, however, this is not the case. Here, the phase transition occurs within the leaf; water evaporates from the cell walls into the air inside the leaf. When the stomata are open, this water then diffuses into the surrounding air. This diffusive water vapor transport, in turn, reduces the water vapor concentration within the leaf (from P_0 to P_1 in Figure 3). The resulting undersaturation within the leaf induces an adiabatic evaporation until a new thermodynamic equilibrium state, P_2, is reached. This adiabatic evaporation component can be described by the psychrometer equation (Eq.

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14), as seen in the thermodynamic derivation of the PM equation. Any additional evaporation within the leaf can only occur through an external supply of energy.

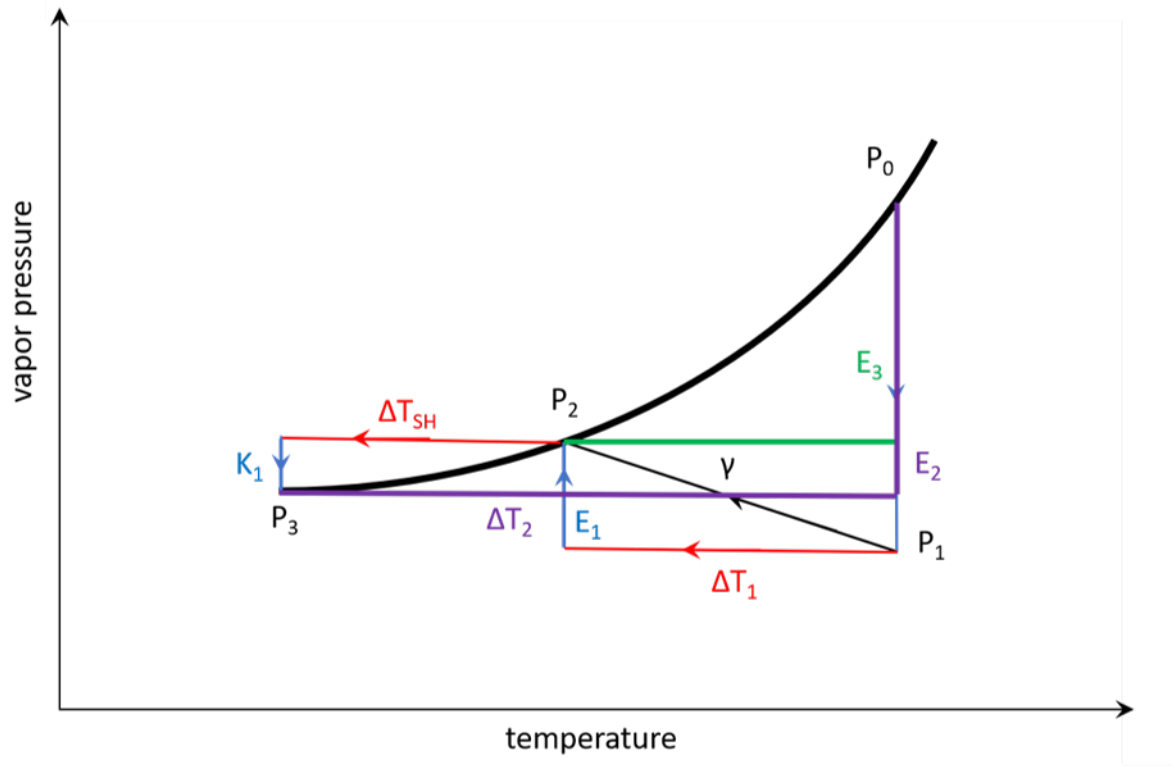

Figure 3: Temperature/water vapor pressure diagram for the evaporation of vegetated surfaces

Unlike an open water surface, however, this external energy supply is not the sensible heat flux from the surface to the adjacent air. In the case of a leaf, this flux is directed outward to the ambient air and not into the air mass where evaporation occurs, namely, the air inside the leaf. Consequently, the sensible heat flux does not represent an external energy supply for the air mass into which evaporation occurs, but rather an energy sink. Thus, the release of sensible heat into the ambient air removes energy from the leaf and the internal leaf air, causing its temperature to decrease. This temperature reduction leads to a decrease in the saturation vapor pressure within the leaf, resulting in net condensation. The condensation rate can be calculated using Eq. (17), albeit with reversed signs, as from a thermodynamical perspective the direction of the phase transition is irrelevant. At P_3, the air mass within the leaf is again saturated. Under steady-state conditions, this release of sensible and latent heat from the leaf must equal the net radiation $R_n - G$ (or equal R_n, assuming that no ground heat flux occurs from a leaf surface (Schymanski & Or, 2017)). That means that the solar energy input increases the energy state of the leaf along the saturation vapor pressure curve from P_3 until the initial state P_0 is reached. Thus, P_0 represents the thermodynamic equilibrium state. P_1,

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P_2 and P_3 are not actual states traversed sequentially during the transformation of solar energy into turbulent heat; rather, they represent potential states that allow the calculation of the transformed energy amounts. The actual energy state of the steady-state leaf is P_0, under which a continuous diffusive water vapor transport induces adiabatic evaporation within the leaf, a sensible heat flux cools the leaf air and triggers condensation, and the absorbed radiation energy increases both the sensible and latent energy level of the leaf air according to the slope of the saturation vapor pressure curve s at P_0.

While in Monteith's (1965) derivation, $E_1 + E_2$ is still equal to the total evaporation E_G (Figure 2), this is no longer the case for a transpiring leaf surface, as clearly shown in Figure 3. Since the external energy input must now compensate for the loss of sensible heat, E_G is given by:

$$E_G = E_1 - K_1 + E_2 \tag{25}$$

where K_1 is the condensation rate that arises from supersaturation caused by the release of sensible heat (in W m^{-2}). The diabatic component of the PM equation (Eq. 18) therefore does not apply to the thermodynamic state change between P_2 and P_0, but rather to the change between P_3 and P_0. To account for the contribution of K_1 to the total evaporation E_G in the PM equation, an additional term would need to be introduced that has the form of Eq. (18), but in which Q represents SH rather than $R_n - G$, and the slope s is negative:

$$\lambda E_G = \frac{s(R_n-G)}{s+\gamma} + \frac{\rho_a c_{pa}(e_{P0}-e_{P1})/r_a}{s+\gamma} - \frac{s(SH)}{s+\gamma} \tag{26}$$

However, Figure 3 also shows that, regardless of K_1, the following must always hold:

$$E_G = E_1 + E_3 \tag{27}$$

For this relationship, Eq. (21) remains valid, and the calculation of λE_1 can still be approximated by the adiabatic component from the PM equation (Eq. 22). According to Figure 3, E_3 is then obtained as follows:

$$E_3 = E_1 * \frac{s}{\gamma} \tag{28}$$

By dividing E_1 by γ, ΔT_1 is obtained, and multiplying this by s yields the partial diabatic component E_3. This relationship can now be combined with Eq. (22) and inserted into Eq. (27):

$$\lambda E_G = \frac{\rho_a c_{pa}(e_{P0}-e_{P1})/r_a}{s+\gamma} + \left(\frac{\rho_a c_{pa}(e_{P0}-e_{P1})/r_a}{s+\gamma}\right)\frac{s}{\gamma} \tag{29}$$

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Further simplification yields:

$$\lambda E_G = \frac{\rho_a c_{pa}(e_{P0}-e_{P1})/r_a}{s+\gamma}\left(1+\frac{s}{\gamma}\right) \quad (30)$$

In analogy with Monteith's (1965) thermodynamic derivation, $e_{P0} - e_{P1}$ represents the saturation vapor pressure deficit inside the leaf which arises from the diffusion of water vapor through the stomata, i.e., the moisture potential of the air mass into which the phase transition occurs. Equations (26) and (30) thus constitute thermodynamically consistent forms of the Penman-Monteith equation that are adapted to vegetated surfaces.

However, the saturation deficit of the air mass into which evaporation occurs no longer depends on the ambient air temperature, as was the case in the original derivations by Penman (1948) and Monteith (1965), but rather on the leaf temperature. The thermodynamically corrected forms of the PM equation can therefore no longer be solved using variables that are obtained from standard measurements at weather stations. This correction consequently eliminates the major advantage that the PM equation has over other methods.

Thus, Eqs. (26) and (30) can be further simplified. If, in Eq. (26), the sensible heat flux SH is replaced by $R_n - G - \lambda E_G$ according to Eq. (1) and the equation is then solved for λE_G, the result is:

$$\lambda E_G = \frac{\rho_a c_{pa}(e_{P0}-e_{P1})}{\gamma r_a} \quad (31)$$

In this context, γr_a can be expressed as the reciprocal of the transfer coefficient $c_{\lambda E}$ and consequently corresponds to Eq. (1). Likewise, Eq. (30) can be further simplified to Eq. (31) or, equivalently, to Eq. (1). The thermodynamic derivation of the PM equation is therefore internally consistent, so that the conclusions derived from it can also be transferred to the classical derivation of the PM equation: (1) A thermodynamically consistent description of evaporation that does not require explicit consideration of surface conditions is possible only for saturated and unvegetated surfaces. (2) The approximation of the ratio of constructed spatial potential differences by s_{Ta} and the associated partitioning of $R_n - G$ as proposed by Penman (1948) is not valid for vegetated surfaces. (3) The Penman-Monteith equation can therefore only be applied in its original form (Penman, 1948) to water saturated and unvegetated surfaces.

5 Conclusions

The Penman-Monteith equation is the most widely used method for estimating evaporation from vegetated surfaces. In Penman's (1948) classic derivation, evaporation is obtained indirectly from the surface energy balance by approximating the

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sensible heat flux. For this approximation, Penman (1948) relates the spatial temperature difference between the surface and the near-surface air, which drives the sensible heat flux, to the difference in saturation vapor pressure at the surface and in the air and approximates this constructed relationship by the slope of the saturation vapor pressure curve for the air temperature s_{Ta}. In its proper sense, however, s_{Ta} describes the thermodynamic state change of saturated air when energy is added, that is, how the system's heat and moisture content evolve. By contrast, $T_s - T_a$ does not represent the temperature change of the system but a spatial potential difference. Consequently, s_{Ta} is not used to describe thermodynamic state changes; rather, it is employed to approximate the ratio of hypothetical spatial potential differences between two distinct systems.

In his thermodynamic derivation of the Penman-Monteith equation, however, Monteith (1965) found a way to circumvent this step by describing the evaporation process as a combination of two sub-processes: an adiabatic component, in which evaporation is induced by the initial undersaturation of the air, and a diabatic component, in which any further evaporation can occur only through the warming of the saturated air and the associated increase in saturation vapor pressure. By doing so, Monteith (1965) is able to describe evaporation without spatial potential differences and to explain the introduction of s_{Ta} through the thermodynamic state change of the near-surface air in a physically consistent manner.

From a mathematical point of view, s_{Ta} is first employed in the Penman-Monteith equation to partition the available energy at the surface, $R_n - G$. In this context, s_{Ta} describes how an energy input into the air, in which evaporation takes place, is divided into sensible and latent heat fluxes. In order to use s_{Ta} for this purpose, the ratio of SH to λE must be equal to the change in the air's saturation vapor pressure caused by a temperature change. However, this condition is only met when the sensible heat flux from the surface raises the temperature of the air into which the phase transition occurs. In that case, the sensible energy input causes the saturation vapor pressure, and thus the resulting evaporation, to change in accordance with s_{Ta}.

However, this applies only to saturated, unvegetated surfaces; it does not hold for vegetated surfaces. During the transpiration process the phase transition takes place inside the leaf. For the air within a leaf, the sensible heat flux that is directed toward the atmosphere does not represent an energy input but rather an energy sink. Thus, the sensible heat flux does not directly induce a latent heat flux into the saturated air, and therefore s_{Ta} cannot be used to partition $R_n - G$. In terms of the applicability of the Penman-Monteith equation, this means that the approximation of the ratio of spatial potential differences by s_{Ta} can only be physically justified for saturated, unvegetated surfaces, and the equation is consequently only valid under such conditions. Hence, the Penman-Monteith equation is not applicable to vegetated surfaces.

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Variables and Symbols

R_n	net radiation	W m^{-2}
G	ground heat flux	W m^{-2}
SH, λE	sensible, latent heat flux	W m^{-2}
c_{SH}, $c_{\lambda E}$	transfer coefficient for SH and λE	m s^{-1}
$T_{s,a}$	temperature at the surface, air	K
$e_{s,a,d}$	vapor pressure at surface, air, saturated air at T_a	Pa
β	Bowen ratio	-
γ	psychrometric constant	Pa K^{-1}
s, s_{Ta}	slope of the saturation vapor pressure curve	Pa K^{-1}
λ	latent heat of water vapor	J kg^{-1}
$E_{G,1,2,3}$	total, adiabatic, diabatic evaporation	kg m^{-2} s^{-1}
$\Delta T_{1,2}$	adiabatic, diabatic temperature difference	K
K_1	condensation rate	kg m^{-2} s^{-1}
p_a	atmospheric pressure	Pa
ρ_a	density of dry air	kg m^3
c_{pa}	heat capacity of air	J kg^{-1} K^{-1}
$r_{a,s}$	aerodynamic and stomata resistance	s m^{-1}

Code and data availability

This is a purely theoretical work for which no code was written and no data was analyzed.

Competing interests

The author has declared that he has no competing interests.

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