

Entropy Budget of an Atmosphere in Radiative–Convective Equilibrium. Part II: Latent Heat Transport and Moist Processes

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ABSTRACT

In moist convection, atmospheric motions transport water vapor from the earth's surface to the regions where condensation occurs. This transport is associated with three other aspects of convection: the latent heat transport, the expansion work performed by water vapor, and the irreversible entropy production due to diffusion of water vapor and phase changes. An analysis of the thermodynamic transformations of atmospheric water yields what is referred to as the entropy budget of the water substance, providing a quantitative relationship between these three aspects of moist convection. The water vapor transport can be viewed as an imperfect heat engine that produces less mechanical work than the corresponding Carnot cycle because of diffusion of water vapor and irreversible phase changes.

The entropy budget of the water substance provides an alternative method of determining the irreversible entropy production due to phase changes and diffusion of water vapor. This method has the advantage that it does not require explicit knowledge of the relative humidity or of the molecular flux of water vapor for the estimation of the entropy production. Scaling arguments show that the expansion work of water vapor accounts for a small fraction of the work that would be produced in the absence of irreversible moist processes. It is also shown that diffusion of water vapor and irreversible phase changes can be interpreted as the irreversible counterpart to the continuous dehumidification resulting from condensation and precipitation. This leads to a description of moist convection where it acts more as an atmospheric dehumidifier than as a heat engine.

1. Introduction

In a companion paper (Pauluis and Held 2002), it is argued that a large fraction of the irreversible entropy production in a moist atmosphere in radiative–convective equilibrium results from diffusion of water vapor and irreversible phase changes. As a consequence, the work performed by convective systems is significantly smaller than what is predicted by theories based on a perfect heat engine framework such as Rennó and Ingersoll (1996) and Emanuel and Bister (1996).

A key argument in Pauluis and Held (2002) is that moist convection acts not only as a heat engine, but also as an atmospheric dehumidifier that continuously re-

moves water vapor from moist air through condensation and precipitation. The present paper further investigates this notion of atmospheric dehumidifier and its relationship to latent heat transport.

In an atmosphere in radiative–convective equilibrium, convective motions generate an upward transport of water vapor that is balanced by a net downward flux of condensed water. For simplicity, we limit our discussion to a case where all condensed water is liquid. Any mass transport is also associated with an energy transport equal to the mass transport multiplied by the specific enthalpy of the corresponding fluid. The specific enthalpy of liquid water is given by $h_l = C_l T$, with C_l the specific heat of liquid water, and T the temperature. The specific enthalpy of water vapor is $h_v = C_l T + L_v$ where $L_v = h_v - h_l$ is the latent heat of vaporization. The combination of an upward transport of water vapor and downward transport of liquid water is associated with a net upward transport of latent heat approximately equal to $\int_{z=z_0} L_v \rho q_v w$. Here, ρ is the total mass of air per unit volume, q_v is the specific humidity, and w is the vertical velocity of air. The integral is performed on a horizontal surface. Atmospheric motions transport la-

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tent heat from the earth's surface to the regions where the latent heat is released through condensation.

Because latent heat is transported from a warm surface to colder regions, Carnot's heat engine analogy comes to mind. The total amount of work produced by water vapor is given by

$$W_{\text{vap}} = \int_{\Omega} e \partial_i V_i. \quad (1)$$

Here, \int_{Ω} indicates the integral over the whole atmospheric domain, e is the water vapor pressure, V_i is the i th component of velocity, $\partial_i = \partial/\partial x_i$ denotes the partial derivative in the i th direction, and the convention of summing over repeated indices is used. In the classic Carnot cycle, work is produced by a combination of a warm expansion and cold compression. In contrast, the work performed by water vapor results primarily from its expansion during its ascent: the condensed water, being incompressible, does not require any compression work to be brought to the surface. This explains that although water vapor accounts for less than 2% of the total mass of the atmosphere, it may produce a large fraction of the total work, as observed in the simulations of Pauluis and Held (2002).

A heat transport from a warm source to a cold sink does not necessarily involve the production of mechanical work. Consider for instance a dehumidifier working at constant volume. An initial mass of saturated air is cooled so that water vapor condenses. The air is then warmed and brought back to its initial temperature, without allowing any reevaporation. The initial parcel of moist air can be reformed by evaporating the liquid water at constant temperature. These transformations are performed at constant volume, and no work is performed on or by the system during the cycle. As heating occurs at a warmer temperature than cooling, the heat exchanges with the environment result in a net export of entropy out of the system. This loss of entropy is balanced by the entropy production due to the irreversible evaporation. In an alternative version of this cycle, the evaporation occurs in a separate chamber containing saturated air at the same temperature and pressure, and water vapor diffuses from this chamber into the dry air. From a thermodynamic perspective, the only difference with the original cycle is that the irreversible entropy production results from diffusion of water vapor instead of irreversible evaporation. In both versions, the cooling of moist air and warming of dry air acts as a reversible dehumidifier. It is followed by an irreversible moistening of dry air, associated at the microphysical level with either an irreversible phase change or a diffusion of water vapor.

The diffusion of mass δM of water vapor from a region at water vapor pressure e_1 to a region at water vapor pressure e_2 results in an irreversible entropy production given by

$$\Delta S_{\text{irr}} = R_v \delta M \ln \frac{e_1}{e_2}, \quad (2)$$

with R_v the gas constant of water vapor. The second law of thermodynamics requires diffusion to occur from high water vapor pressure to low water vapor pressure. The irreversible entropy production due to the evaporation of a quantity δM of water into air at relative humidity $\mathcal{H} = e/e_s$, with e_s the saturation water vapor pressure, is given by

$$\Delta S_{\text{irr}} = -R_v \delta M \ln \mathcal{H}. \quad (3)$$

Phase changes at saturation ($\mathcal{H} = 1$) are reversible while condensation of supersaturated water vapor ($\delta M < 0$ and $\mathcal{H} > 1$) and evaporation of condensed water in unsaturated air ($\delta M > 0$ and $\mathcal{H} < 1$) are irreversible and result in a production of entropy $\Delta S_{\text{irr}} > 0$.

Comparing (2) and (3) shows that the entropy production due to irreversible evaporation is the same as the production resulting from the combination of reversible evaporation followed by diffusion of water vapor from the saturation water vapor pressure to the ambient vapor pressure. The distinction between the two processes is somewhat arbitrary and depends on the behavior of the interface between condensed water and moist air. However, the total entropy production due to diffusion of water vapor and irreversible phase changes is independent of the specific representation. For this reason, we focus primarily on the total irreversible entropy production due to moist processes, that is, the sum of entropy production by irreversible phase changes and diffusion of water vapor.

The expressions of the irreversible entropy production in (2) and (3) can be extended to a moist atmosphere by assuming that moist air behaves as an ideal mixture of ideal gases [for a derivation of the entropy production in multiphase systems, see De Groot (1951)]. The irreversible entropy production by diffusion of water vapor for the whole atmosphere is

$$\Delta S_{\text{dv}} = \int_{\Omega} -R_v J_{v,i} \partial_i \ln e, \quad (4)$$

where $J_{v,i}$ is the i th component of the molecular flux of water vapor, and e is the partial pressure of water vapor. If we limit ourselves to phase transitions between water vapor and liquid water, the total irreversible entropy production due to phase changes is

$$\Delta S_{\text{pc}} = \int_{\Omega} (C - E) R_v \ln \mathcal{H} - \int_{z=0} J_{v,z} R_v \ln \mathcal{H}. \quad (5)$$

Here, C and E are the condensation and evaporation rates per unit volume, and $J_{v,z}$ is the vertical component of the molecular flux of water vapor. The first term on the right-hand side is the production due to irreversible condensation and reevaporation in the atmosphere. The second term is the production due to irreversible evaporation at the surface.

In moist convection, the transport of water vapor—and the corresponding latent heat transport—can be thought of as acting partially as a heat engine and partially as an atmospheric dehumidifier. The expansion work performed by water vapor W_{vap} is a measure of how much the latent heat transport acts as a heat engine. As condensation and precipitation continuously remove water vapor, moist convection also acts as an atmospheric dehumidifier. In statistical equilibrium, the dry air outflow from convective towers must be moistened again. This moistening is associated with various processes such as mixing of cloud and environmental air, reevaporation of precipitation, entrainment in the planetary boundary layer and surface evaporation. All these processes are irreversible and associated at the microphysical level with diffusion of water vapor or irreversible phase changes. Hence, the entropy production due to the moist processes $\Delta S_{\text{dv}} + \Delta S_{\text{pc}}$ can be viewed as a measure of the strength of the dehumidification associated with the latent heat transport.

In the next section, we look in more detail at the thermodynamic transformations undergone by water in moist convection. A formulation for the local rate of change of the entropy of water vapor and liquid water is first derived. This local formulation is then integrated over the whole atmosphere. This yields a relationship between latent heat transport, expansion work of water vapor and irreversible entropy production due to moist processes. This relationship, which we will refer to as the *entropy budget of the water substance*, allows us to determine the entropy production due to diffusion of water vapor and irreversible phase changes from the latent heat flux and expansion work of water vapor without requiring the local knowledge needed by the expressions (4) and (5).

Section 3 introduces some scaling arguments for the expansion work of water vapor and the latent heat transport. It is shown that most of the entropy increase due to latent heat transport can be attributed to diffusion of water vapor and irreversible phase changes. In section 4, we argue in more detail that the irreversible entropy production due to diffusion of water vapor and irreversible phase changes can be viewed as the irreversible counterpart to a reversible dehumidification associated with condensation and precipitation. Section 5 discusses how the strength of the latent heat transport can be modified by reevaporation in the atmosphere. A final section presents our conclusion on the importance of the hydrological cycle for our understanding of the entropy budget of moist convection.

2. Entropy budget of the water substance

a. Local variation of entropy

Because the expressions for the entropy sources due to diffusion and phase changes are unfamiliar to many, we derive these from the familiar equations in fluid

dynamics. This derivation yields Eq. (17). Readers who accept this equation may wish to skip this section.

We consider here the thermodynamic transformations of water during moist convection and derive the corresponding changes of entropy. Water in all phases is treated here as a distinct subsystem within the atmosphere. This subsystem can be viewed as continuously exchanging heat with and performing work on the surrounding dry air. By focusing on water alone, it is possible to isolate the thermodynamic processes directly related to water: latent heat transport by convection, expansion work performed by water vapor, phase changes and diffusion of water vapor.

For simplicity, we limit ourselves to water vapor and liquid water only. The continuity equations for water vapor and liquid water are

$$\partial_t(\rho q_v) + \partial_i(\rho q_v V_i + J_{v,i}) = E - C \quad (6)$$

$$\partial_t \rho q_l + \partial_i(\rho q_l V_i) + \partial_z(\rho q_l V_T) = C - E, \quad (7)$$

with V_T the falling velocity of the condensed water relative to the surrounding air.

The specific entropy of liquid water is given by $s_l = C_l \ln T$, and the specific entropy of water vapor is $s_v = C_l \ln T + L_v/T - R_v \ln \mathcal{H}$. The total entropy of the water substance per unit volume is given by $\rho q_v s_v + \rho q_l s_l$. The rate of change of the entropy of water substance per unit volume δS is given by

$$\begin{aligned} \delta S = & \partial_t(\rho q_v s_v + \rho q_l s_l) + \partial_i(\rho q_v V_i s_v + \rho q_l V_i s_l) \\ & + \partial_i(J_{v,i} s_v) + \partial_z(\rho q_l V_T s_l). \end{aligned} \quad (8)$$

When integrated over a small volume, the first term on the right-hand side of this equation becomes the net change of entropy; the second term yields the export of entropy by the atmospheric flow; the third term is the export through molecular diffusion of water vapor; and the fourth term is the export through falling precipitation.

Using the continuity equations for water vapor and liquid water (6) and (7), (8) becomes

$$\delta S = \rho q_v \frac{d_v}{dt} s_v + \rho q_l \frac{d_l}{dt} s_l + (E - C)(s_v - s_l). \quad (9)$$

Here, $d_v/dt = \partial_t + V_i \partial_i + (\rho q_v)^{-1} J_{v,i} \partial_i$ denotes the Lagrangian derivative following the motion of water vapor, and $d_l/dt = \partial_t + V_i \partial_i + V_T \partial_z$ is the Lagrangian derivative following the motion of liquid water.

Variations of the specific entropies of water vapor and liquid water are given by the following thermodynamic relationships:

$$\frac{d_v}{dt} s_v = \frac{1}{T} \frac{d_v}{dt} h_v - \frac{\alpha_v}{T} \frac{d_v}{dt} e \quad (10)$$

$$\frac{d_l}{dt} s_l = \frac{1}{T} \frac{d_l}{dt} h_l. \quad (11)$$

Here, $\alpha_v = (\rho q_v)^{-1} = R_v T/e$ is the specific volume of

water vapor, $h_l = C_l T$ is the specific enthalpy of liquid water, and $h_v = C_l T + L_v$ is the specific enthalpy of water vapor. The specific volume of liquid water has been neglected in (11).

In addition, the entropy change associated with phase transition can be written as

$$\begin{aligned} (E - C)(s_v - s_l) &= (E - C)\frac{L_v}{T} - (E - C)R_v \ln \mathcal{H} \\ &= (E - C)\frac{L_v}{T} + \delta S_{pc}, \end{aligned} \quad (12)$$

where $\delta S_{pc} = -(E - C)R_v \ln \mathcal{H}$ is the entropy production due to irreversible phase changes. Combining (10), (11), and (12) into (9) yields

$$\begin{aligned} \delta S &= \rho q_v \frac{1}{T} \frac{d_v}{dt} h_v + \rho q_l \frac{1}{T} \frac{d_l}{dt} h_l + (E - C)\frac{L_v}{T} \\ &\quad - \frac{1}{T} \frac{d_v}{dt} e + \delta S_{pc}. \end{aligned} \quad (13)$$

The first three terms on the right-hand side of this equation are the entropy variations resulting from changes in enthalpy. Using the continuity equations (6) and (7) yields

$$\rho q_v \frac{1}{T} \frac{d_v}{dt} h_v + \rho q_l \frac{1}{T} \frac{d_l}{dt} h_l + (E - C)\frac{L_v}{T} = \frac{\delta H}{T}, \quad (14)$$

where δH is the rate of change of enthalpy of water substance per unit volume:

$$\begin{aligned} \delta H &= \partial_t(\rho q_v h_v + \rho q_l h_l) + \partial_t(\rho q_v V_i h_v + \rho q_l V_i h_l + J_{v,i} h_v) \\ &\quad + \partial_z(\rho q_l h_l V_T). \end{aligned} \quad (15)$$

The contribution of the water vapor pressure change in (13) can be written as

$$\begin{aligned} -\frac{1}{T} \frac{d_v}{dt} e &= -\frac{\partial_t e + V_i \partial_i e}{T} - \frac{\alpha_v}{t} J_{v,i} \partial_i e \\ &= -\frac{\partial_t e + V_i \partial_i e}{T} - R_v J_{v,i} \partial_i \ln e \\ &= -\frac{\partial_t e + V_i \partial_i e}{T} + \delta S_{dv}, \end{aligned} \quad (16)$$

where $\delta S_{dv} = -R_v J_{v,i} \partial_i \ln e$ is the irreversible entropy production by diffusion of water vapor. The quantity $-V_i \partial_i e = -\partial_i(V_i e) + e \partial_i V_i$ is the total work per unit volume due to the water vapor pressure. It is the sum of the external work $-\partial_i(V_i e)$ and the internal (expansion) work $e \partial_i V_i$. Notice that the quantity $T \delta S_{dv} = \alpha_v J_{v,i} \partial_i e$ is the additional amount of work that would have been performed by water vapor if the velocity of the flow had been $V_i + \alpha_v J_{v,i}$ instead of V_i .

Combining (14) and (16) into (13) yields the expression for the change of the entropy of the water substance:

$$\delta S = \frac{\delta H}{T} - \frac{\partial_t e + V_i \partial_i e}{T} + \delta S_{pc} + \delta S_{dv}. \quad (17)$$

Notice that $\delta H + \partial_t e + V_i \partial_i e = \delta Q$ is the amount of heat that the water substance receives from its environment (mostly though exchange with the surrounding dry air):

$$\begin{aligned} \delta Q &= \delta H + \partial_t e + V_i \partial_i e \\ &= \partial_t[\rho q_v(h_v - \alpha_v e) + \rho q_l h_l] \\ &\quad + \partial_i(\rho q_v V_i h_v + \rho q_l V_i h_l + J_{v,i} h_v) \\ &\quad + \partial_z(\rho q_l h_l V_T) - e \partial_t v. \end{aligned} \quad (18)$$

The first term on the right-hand side is the rate of change of the internal energy of the water per unit volume. The second and third terms are the energy (enthalpy) transport due to motion, diffusion, and precipitation. The fourth term is the work performed by water vapor. Equation (18) can thus be viewed as a local formulation of the first law of thermodynamics for the water substance. Equation (17) can be written as

$$\delta S = \frac{\delta Q}{T} + \delta S_{pc} + \delta S_{dv}. \quad (19)$$

Hence, (17) is the local formulation of the second law of thermodynamics for the water substance.

b. Entropy budget of water substance

The entropy budget of all the water contained in an atmosphere is obtained by integrating (17) over the whole atmospheric domain Ω :

$$\int_{\Omega} \delta S = \int_{\Omega} \left(\frac{\delta H}{T} - \frac{\partial_t e + V_i \partial_i e}{T} + \delta S_{dv} + \delta S_{pc} \right). \quad (20)$$

We discuss now this entropy budget for an atmosphere in radiative-convective equilibrium.

The left-hand side of (20) is the total entropy change of water. Water is added to the atmosphere through evaporation at the surface, and is removed through precipitation. The total entropy change of water is equal to the entropy change resulting from the transformation of the water vapor inflow into liquid water:

$$\begin{aligned} \int_{\Omega} \delta S &= P(s_{l,\text{surf}} - s_{v,\text{surf}}) \\ &= -P \frac{L_{v0}}{T_{\text{surf}}} + PR_v \ln \mathcal{H}_{\text{surf}} \\ &= -\frac{Q_{\text{lat}}}{T_{\text{surf}}} + PR_v \ln \mathcal{H}_{\text{surf}}, \end{aligned} \quad (21)$$

where P is the precipitation rate, $s_{l,\text{surf}}$ and $s_{v,\text{surf}}$ are the specific entropies of liquid water and water vapor at the surface, L_{v0} is the latent heat of vaporization at the surface temperature, $\mathcal{H}_{\text{surf}}$ is the relative humidity at the

surface, and $Q_{\text{lat}} = L_{v0}P$ is the latent heat flux at the surface. The second term on the right-hand side is minus the entropy production due to irreversible evaporation at the surface.

The first term on the right-hand side of (20) is the entropy change associated with enthalpy change. For simplicity, we neglect the specific heat of liquid water and water vapor. In this case, the enthalpy change of a water parcel is equal to the change of its latent heat content:

$$\delta H \approx L_{v0}(E - C). \quad (22)$$

To be consistent with the approximation $C_l \approx C_{pv} \approx 0$, the latent heat of evaporation has to be independent of temperature. It is chosen to be equal to its value at the sea surface temperature L_{v0} to ensure that the latent heat flux at the surface is equal to the total latent heat release in the atmosphere: $Q_{\text{lat}} = \int_{\Omega} L_{v0}(C - E)$. The first term on the right-hand side becomes

$$\int_{\Omega} \frac{\delta H}{T} \approx - \int_{\Omega} \frac{L_{v0}(C - E)}{T} = - \frac{Q_{\text{lat}}}{T_{\text{lat}}}. \quad (23)$$

The *effective temperature of latent heat release* T_{lat} is defined by

$$T_{\text{lat}} = Q_{\text{lat}} \left(\int_{\Omega} \frac{L_{v0}(C - E)}{T} \right)^{-1}. \quad (24)$$

For a closed system in statistical equilibrium, the expansion work of water vapor can be written as

$$W_{\text{vap}} = \int_{\Omega} e \partial_i V_i = - \int_{\Omega} \partial_i e + V_i \partial_i e. \quad (25)$$

The second term on the right-hand side of (20) can be written as

$$- \int_{\Omega} \frac{\partial_i e + V_i \partial_i e}{T} = \frac{W_{\text{vap}}}{T_{\text{vap}}}. \quad (26)$$

The *effective temperature of vapor pressure change* T_{vap} is defined by

$$T_{\text{vap}} = -W_{\text{vap}} \left(\int_{\Omega} \frac{\partial_i e + V_i \partial_i e}{T} \right)^{-1}. \quad (27)$$

Using (21), (23), and (26) in (20) yields the entropy budget of the hydrological cycle:

$$\frac{Q_{\text{lat}}}{T_{\text{surf}}} - \frac{Q_{\text{lat}}}{T_{\text{lat}}} + \frac{W_{\text{vap}}}{T_{\text{vap}}} + \Delta S_{\text{dv}} + \Delta S_{\text{pc}} = 0. \quad (28)$$

This is a fundamental relationship between the latent heat transport Q_{lat} , expansion work of water vapor W_{vap} , and the irreversible entropy production due to moist processes $\Delta S_{\text{dv}} + \Delta S_{\text{pc}}$. Expression (28) can be interpreted as the entropy budget of a heat engine as illustrated in Fig. 1. This heat engine carries an amount of heat Q_{lat} from the surface to the condensation region. The entropy source associated with surface evaporation

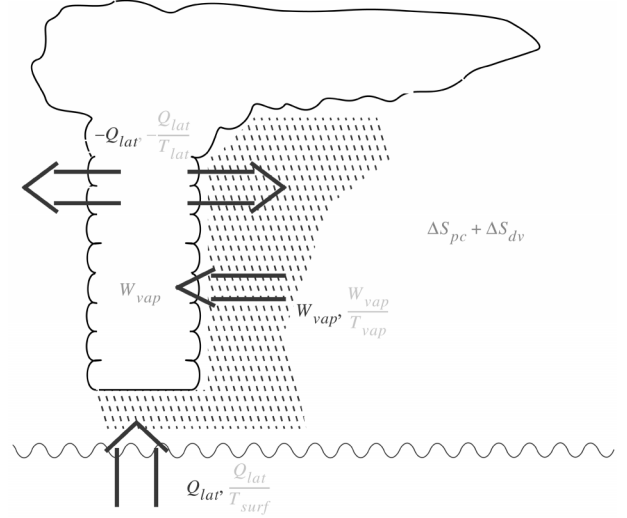


FIG. 1. Representation of the latent heat transport as an imperfect heat engine. Here, Q_{lat} is the latent heat received at the surface and released in the troposphere, W_{vap} is the mechanical work due to water vapor expansion, and ΔS_{dv} and ΔS_{pc} are the irreversible entropy productions due to diffusion of water vapor and to irreversible phase changes.

is $Q_{\text{lat}}/T_{\text{surf}}$. The entropy sink associated with latent heat release is $Q_{\text{lat}}/T_{\text{lat}}$. The heat engine also performs an amount of work W_{vap} on its environment. Conservation of energy requires this mechanical work to be compensated for by an additional heat source, which occurs at the effective temperature T_{vap} . This additional heat source is associated with an entropy source $W_{\text{vap}}/T_{\text{vap}}$. Finally, irreversible phase changes and diffusion of water vapor result in an irreversible entropy production $\Delta S_{\text{dv}} + \Delta S_{\text{pc}}$. The entropy budget (28) requires these various entropy sources and sinks to balance each other.

One can define W_{lat} as the amount of work that would be produced by water vapor in the absence of irreversible moist processes:

$$W_{\text{lat}} = Q_{\text{lat}} T_{\text{vap}} \left(\frac{1}{T_{\text{lat}}} - \frac{1}{T_{\text{surf}}} \right). \quad (29)$$

This is the amount of work that would be produced if the latent heat is transported by a perfect heat engine. It can also be viewed as a measure of the thermodynamic action of the latent heat transport. The difference between the maximum work W_{lat} and the work effectively done by water vapor expansion W_{vap} results from the loss of mechanical work due to irreversible phase changes and diffusion of water vapor:

$$\Delta S_{\text{dv}} + \Delta S_{\text{pc}} = \frac{W_{\text{lat}} - W_{\text{vap}}}{T_{\text{vap}}}. \quad (30)$$

Alternatively, Eq. (30) allows one to determine the irreversible entropy production from the latent heat transport and expansion work by water vapor, *without requiring explicit knowledge of the molecular flux of water*

vapor or of the relative humidity at condensation and reevaporation.

3. Scaling for the entropy budget of the water substance

If the production of mechanical work by water vapor is equal to the maximum work that could be produced by the latent heat transport, there is no irreversible entropy production due to diffusion of water vapor and phase changes. Conversely, if the expansion work by water vapor is much smaller than the maximum work, then there is a significant irreversible entropy production due to moist processes.

In the appendix, Eq. (A5), it is shown that the contribution of vapor pressure changes in (28) can be approximated by

$$\frac{W_{\text{vap}}}{T_{\text{vap}}} \approx \int_{\Omega} g \frac{R_v}{R_d T} \bar{\rho} w q_v. \quad (31)$$

As shown in the appendix, this is obtained after making the approximation $\partial_z p + V_z \partial_z p \approx w \partial_z \bar{p}$.

Consider now that convection transports water vapor from the surface to the mean condensation level h_c . The entropy contribution associated with vapor pressure changes can be approximated by

$$\frac{W_{\text{vap}}}{T_{\text{vap}}} \approx g \frac{R_v}{R_d T} P h_c. \quad (32)$$

where \bar{T} is a typical tropospheric temperature. In this scaling, the temperature variations T' in the troposphere are assumed to be small in comparison to the absolute temperature, and the high-order terms in T'/\bar{T} are neglected.

The maximum work associated with the latent heat transport (29) is

$$\frac{W_{\text{lat}}}{T_{\text{vap}}} = Q_{\text{lat}} \left(\frac{1}{T_{\text{lat}}} - \frac{1}{T_{\text{surf}}} \right) \approx L_{v0} P \frac{T_{\text{surf}} - T_{\text{lat}}}{\bar{T}^2}. \quad (33)$$

Hence, the ratio between water vapor expansion and the maximum work is

$$\begin{aligned} \frac{W_{\text{vap}}}{W_{\text{lat}}} &\approx \left(\frac{R_v}{R_d} g h_c \right) / \left(L_{v0} \frac{T_{\text{surf}} - T_{\text{lat}}}{\bar{T}} \right) \\ &\approx \left(\frac{g}{R_d T} \right) / \left(-\frac{L_{v0} \partial_z T}{R_v T^2} \right), \end{aligned} \quad (34)$$

where we set $(T_{\text{lat}} - T_{\text{surf}})/h_c = \partial_z T$, that is, the average lapse rate between the surface and the condensation level. The numerator on the right-hand side of (34) is equal to $H_p^{-1} = -\partial_z \ln p = g/R_d T$ where H_p is the pressure scale height. The denominator is equal to $H_{e_s}^{-1} = -\partial_z \ln e_s = -L_{v0} \partial_z T / R_v T^2$, where H_{e_s} is the scale height for the saturation vapor pressure.

The ratio of the expansion work by water vapor to the maximum work that could be done by the latent heat

transport is approximately equal to the ratio between the saturation vapor pressure scale height and the pressure scale height

$$W_{\text{vap}} \approx \frac{H_{e_s}}{H_p} W_{\text{lat}}. \quad (35)$$

The difference between the effective work and the maximum work must be accounted for by the irreversible entropy production due to moist processes. Combining (30) and (35) yields

$$\Delta S_{\text{dv}} + \Delta S_{\text{pc}} \approx \left(1 - \frac{H_{e_s}}{H_p} \right) \frac{W_{\text{lat}}}{T_{\text{vap}}}. \quad (36)$$

For the tropical atmosphere, the pressure scale height is about 8 km, and the saturation vapor pressure scale height varies between 1.5 and 2.5 km. These scalings indicate that the work done by water vapor expansion produces only 20%–30% of the work of a perfect heat engine that would transport the latent heat, while the irreversible entropy production due to phase changes and diffusion of water vapor accounts for 70%–80% of the thermodynamic action associated with the latent heat transport.

4. Irreversible entropy production and dehumidification

It may seem surprising that one could determine the irreversible entropy production by phase changes and diffusion of water vapor without requiring knowledge of the molecular flux of water vapor or of relative humidity. This may be better understood if one considers the relationship between these irreversible moist processes and dehumidification. Consider a parcel of saturated air at cloud base. This parcel ascends in an updraft and loses most of its water vapor through condensation and precipitation. Suppose now that this parcel subsides in the free troposphere, without the addition of any water vapor. As its temperature increases while its specific humidity is unchanged, the parcel becomes unsaturated. The transformations leading to this dehumidification are mostly reversible—at least in the context of this simple discussion. Conservation of water vapor implies that the specific humidity can only be increased by evaporation or diffusion of water vapor from moister air. Hence, adding water vapor to an unsaturated parcel of moist air is always an irreversible process. The irreversibility is associated at the microphysical level with either diffusion or evaporation. Convection acts as a continuous supply of dry air. In radiative–convective equilibrium, this dehumidification must be balanced by a continuous moistening of dry air, which involves diffusion of water vapor or reevaporation. We now show that expression (30) can be viewed as determining the irreversible entropy production resulting from such moistening.

In a statistically steady system, conservation of water

vapor implies that the net condensation at a given level is equal to the convergence of the convective transport of water vapor:

$$\partial_z \overline{\rho w q_v} = \overline{E} - \overline{C}. \quad (37)$$

Here, the overline indicates a horizontal average. In this equation, we neglect the vertical transport of water vapor resulting from molecular diffusion. Using the hydrostatic balance $g/R_d T = -\partial_z \ln p$ in Eq. (31) yields

$$\begin{aligned} \frac{W_{\text{vap}}}{T_{\text{vap}}} &\approx - \int_{\Omega} R_v \left(\partial_v \ln \frac{p}{p_{\text{surf}}} \right) \overline{\rho} g w q_v \\ &\approx \int_{\Omega} R_v \ln \frac{p}{p_{\text{surf}}} (\overline{E} - \overline{C}), \end{aligned} \quad (38)$$

where p_{surf} is the surface pressure.

Integrating the Clapeyron–Clausius relationship $d \ln e_s = (L_v/R_v T) dT$ from the surface temperature T_{surf} to a temperature T yields

$$\ln \frac{e_s(T)}{e_s(T_{\text{surf}})} = \frac{L_{v0}}{R_v} \left(\frac{1}{T_{\text{surf}}} - \frac{1}{T} \right), \quad (39)$$

where we have neglected the variations of the latent heat of vaporization. Using this with (29) and (23) gives

$$\begin{aligned} \frac{W_{\text{lat}}}{T_{\text{vap}}} &= \frac{Q_{\text{lat}}}{T_{\text{lat}}} - \frac{Q_{\text{lat}}}{T_{\text{surf}}} = \int_{\Omega} L_{v0} (E - C) \left(\frac{1}{T} - \frac{1}{T_{\text{surf}}} \right) \\ &\approx \int_{\Omega} R_v (E - C) \ln \frac{e_s(T)}{e_s(T_{\text{surf}})}. \end{aligned} \quad (40)$$

Combining (40) and (38) into (30) yields

$$\begin{aligned} \Delta S_{\text{div}} + \Delta S_{\text{pc}} &\approx \int_{\Omega} (E - C) R_v \left(\ln \frac{e_s(T)}{e_s(T_{\text{surf}})} - \ln \frac{p}{p_{\text{surf}}} \right) \\ &\approx \int_{\Omega} R_v (E - C) \ln \frac{q_s(T, p)}{q_{s, \text{surf}}} \\ &\approx R_v P \ln \frac{q_{s, \text{surf}}}{q_{s, \text{cond}}}. \end{aligned} \quad (41)$$

Here, $q_s(T, p)$ is the specific humidity at saturation for a temperature T and total pressure p ; $q_{s, \text{surf}}$ is the saturation specific humidity at the surface; and $q_{s, \text{cond}}$ is the effective saturation humidity at which phase changes occur. In the absence of reevaporation ($E = 0$) $q_{s, \text{cond}}$ is the average specific humidity at condensation. Comparing (41) to (2) indicates that the total entropy production by phase changes and diffusion of water vapor is equal to the irreversible entropy that would be produced by the diffusion, at constant total pressure, of a quantity P of water vapor from a region at specific humidity $q_{s, \text{surf}}$ to a region at specific humidity $q_{s, \text{cond}}$.

The relationship given in (41) can be understood as follows. Assume first that all phase changes are revers-

ible.¹ Condensation and reevaporation result in a net removal of water vapor, which occurs on average at a specific humidity $q_{s, \text{cond}}$. In radiative–convective equilibrium, this removal of water vapor is compensated for by surface evaporation. The latter corresponds to a source of water vapor into air at specific humidity $q_{s, \text{surf}}$. For the system to be in statistical equilibrium, water vapor must be transferred from air parcels at specific humidity $q_{s, \text{surf}}$ to air parcels at specific humidity $q_{s, \text{cond}}$. (If this is not the case, the specific humidity distribution in the atmosphere would change.) However, the specific humidity of a parcel can only be modified through diffusion of water vapor or phase changes. As the latter are already accounted for in $q_{s, \text{cond}}$, water vapor must diffuse from $q_v = q_{s, \text{surf}}$ to $q_v = q_{s, \text{cond}}$. If diffusion occurs at constant total pressure, then the corresponding entropy production is given by (41).

In (41), the left-hand side is the entropy production associated at the microphysical level with diffusion of water vapor and irreversible phase changes. It is equated on the right-hand side to a quantity that measures the amount of dehumidification associated with the latent heat transport. This is equivalent to stating that irreversible phase changes and diffusion of water vapor are such that they balance the atmospheric dehumidification by convection.

5. On the effective temperature of latent heat release

The thermodynamic action resulting from latent heat transport can be measured through the quantity W_{lat} :

$$W_{\text{lat}} + T_{\text{vap}} Q_{\text{lat}} \left(\frac{1}{T_{\text{lat}}} - \frac{1}{T_{\text{surf}}} \right) \approx \frac{T_{\text{surf}} - T_{\text{lat}}}{T} Q_{\text{lat}}. \quad (42)$$

For a given latent heat flux, W_{lat} primarily depends on the difference between the surface temperature T_{surf} and the effective temperature of latent heat release T_{lat} . In the absence of reevaporation ($E = 0$ everywhere), T_{lat} is the harmonic mean condensation temperature. When reevaporation occurs in the atmosphere ($E > 0$ at some location), the term in integral (23) changes sign, and T_{lat} is not an averaged temperature. Instead, one can define a condensation temperature T_C :

$$\frac{Q_C}{T_C} = \int_{\Omega} \frac{L_{v0} C}{T}, \quad (43)$$

and a reevaporation temperature T_E :

$$\frac{Q_E}{T_E} = \int_{\Omega} \frac{L_{v0} E}{T}. \quad (44)$$

Here, $Q_C = \int_{\Omega} L_{v0} C$ is the total latent heat release by condensation, and $Q_E = \int_{\Omega} L_{v0} E$ is the cooling due to

¹ As any irreversible phase change can be treated as a combination of a reversible phase change and diffusion of water vapor, the discussion can easily be extended to cover irreversible phase changes.

reevaporation. As the terms in the integrals (43) and (44) are strictly positive, these two temperatures are the harmonic mean condensation and reevaporation temperatures, and correspond to the temperatures of some parts of the troposphere.

The effective temperature of latent heat release T_{lat} is related to T_C and T_E by

$$\frac{Q_{\text{lat}}}{T_{\text{lat}}} = \frac{Q_C}{T_C} - \frac{Q_E}{T_E} = \frac{Q_{\text{lat}}}{T_C} + Q_E \left(\frac{1}{T_C} - \frac{1}{T_E} \right), \quad (45)$$

where we use $Q_{\text{lat}} = Q_C - Q_E$. Subtracting $Q_{\text{lat}}/T_{\text{surf}}$ in (45) yields the expression for the total latent heat transport:

$$\begin{aligned} \frac{W_{\text{lat}}}{T_{\text{vap}}} &= Q_{\text{lat}} \left(\frac{1}{T_{\text{lat}}} - \frac{1}{T_{\text{surf}}} \right) \\ &= Q_{\text{lat}} \left(\frac{1}{T_C} - \frac{1}{T_{\text{surf}}} \right) + Q_E \left(\frac{1}{T_C} - \frac{1}{T_E} \right). \end{aligned} \quad (46)$$

The latent heat transport can thus be decomposed into a transport of the net latent heat flux Q_{lat} from the surface to the condensation level, and an additional transport of reevaporated water Q_E from the reevaporation level to the condensation level.

The precipitation efficiency ϵ_p is defined as the ratio of the latent heat flux at the surface to the latent heat release by condensation $\epsilon_p = Q_{\text{lat}}/Q_C$. In this case, the latent cooling due to reevaporation is given by $Q_E = Q_{\text{lat}}(1 - \epsilon_p)/\epsilon_p$. Using this expression in (45) yields the expression for the temperature of latent heat release:

$$\begin{aligned} T_{\text{lat}} &= T_C \left(1 + \frac{1 - \epsilon_p}{\epsilon_p} \frac{T_E - T_C}{T_E} \right)^{-1} \\ &\approx T_C + \frac{1 - \epsilon_p}{\epsilon_p} (T_C - T_E). \end{aligned} \quad (47)$$

In the absence of reevaporation $\epsilon_p = 1$, the temperature of latent heat release is equal to the condensation temperature.

When reevaporation occurs at a warmer temperature than condensation, we have $T_E \geq T_C$. The temperature of latent heat release T_{lat} decreases with increasing reevaporation (or decreasing precipitation efficiency). The additional latent heat transport associated with reevaporation reinforces the initial latent heat transport. A stronger latent heat transport is also associated with more expansion work by water vapor and more irreversible entropy production by phase changes and diffusion of water vapor. Conversely, when the reevaporation temperature is lower than the condensation temperature ($T_E \leq T_C$), the temperature of latent heat release increases with increasing reevaporation. The additional latent heat transport associated with reevaporation opposes the initial heat transport and reduces the expansion work of water vapor and the irreversible entropy production due to the moistening effect.

Hence, the influence of reevaporation on the entropy budget depends strongly on the temperature at which it occurs and, thus, on the mechanisms leading to it. For instance, when reevaporation is the result of detrainment of cloud air at cloud top, it occurs at a lower temperature than the temperature at which cloud water condenses during its ascent. Hence, reevaporation at cloud top reduces the total entropy production by diffusion of water vapor and phase changes. Conversely, reevaporation of precipitation usually occurs at a lower level and at a higher temperature than condensation and increases the irreversible entropy production due to moist processes.

The temperature of latent heat release can also be modified by changing the condensation temperature. This can happen in two ways. First, by reducing the relative humidity near the surface, the lifting condensation level (LCL) increases, which leads to a decrease in the condensation temperature. Second, entrainment of midtropospheric air into clouds can modify the level at which condensation occurs in the updraft. An increase of lateral entrainment or a reduction of the midtropospheric relative humidity leads to a lower condensation temperature (condensation occurring on average at a higher level) and thus increases the latent heat transport.

These considerations show that it is difficult to determine a priori the temperature of latent heat release. Many factors can potentially influence it. For example, a change in the external forcing that favors reevaporation of precipitation, such as a stronger cooling in the upper troposphere or a stronger wind shear, could decrease the effective temperature of latent heat release. Conversely, changes that enhance low level, nonprecipitating clouds, such as an increase in the low-level radiative cooling, would reduce T_{lat} .

Nevertheless, it may be possible that the effective temperature of latent heat could be derived from some external constraints. If one could obtain a simple closure for T_{lat} , it would be extremely useful in understanding the entropy budget of convection, as discussed in Pauluis and Held (2002). Consider two extreme, hypothetical examples of such a closure. If enough reevaporation occurs at cloud top or in saturated downdrafts, it is in theory possible to have $T_{\text{lat}} \approx T_{\text{surf}}$. This implies a very weak entropy production due to diffusion of water vapor and phase changes and would be equivalent to the perfect heat engine theories of Rennó and Ingersoll (1996) and Emanuel and Bister (1996). An alternative closure would be to assume that the net latent heat release balances radiative cooling at every level of the atmosphere. Such a closure would result in T_{lat} being equal to the temperature at which the atmosphere is cooled. In this case, moist processes would be the main irreversible entropy source in moist convection. As discussed in Pauluis and Held (2002), a better understanding of the factors determining T_{lat} would lead to a more precise estimate of the entropy budget of moist convection.

6. Conclusions

In this paper, we have shown that three aspects of moist convection, namely latent heat transport, expansion work of water vapor, and atmospheric dehumidification, are closely related to each other. This relationship finds its mathematical expression in Eq. (28), which we refer to as the entropy budget of the water substance.

A first interpretation of this relationship is to view the latent heat transport by moist convection as an inefficient heat engine. The work performed by water vapor is smaller than the maximum theoretical work of a perfect heat engine because of the irreversibilities associated with diffusion of water vapor and irreversible phase changes. Scaling arguments in section 3 show that the mechanical efficiency of the latent heat transport is roughly one-quarter of the mechanical efficiency of a perfect heat engine for current tropical conditions.

A second interpretation is to view moist convection as an atmospheric dehumidifier. Water vapor is continuously removed from the atmosphere through condensation and precipitation. In statistical equilibrium, this removal of water vapor is balanced by evaporation at the surface. However, the sources and sinks of water vapor occur at different specific humidities. In section 4, the irreversible entropy production due to moist processes is related to the strength of atmospheric dehumidification, measured as the ratio of the saturation specific humidity at the surface and the average saturation specific humidity at condensation.

These two views are not contradictory: the hydrological cycle acts partially as a heat engine and partially as an atmospheric dehumidifier. The thermodynamic action of latent heat transport can be measured by W_{lat} , defined as the amount of work if the latent heat were transported by a perfect heat engine. For current conditions, the expansion work of water vapor accounts for about one quarter of this thermodynamic action, while atmospheric dehumidification accounts for the remaining three quarters.

The thermodynamic action of the latent heat transport depends primarily on the total latent heat transport and on the difference between the surface temperature and the effective temperature of latent heat release. In section 5, it is shown that this effective temperature is difficult to determine from first principles as it depends on the various microphysical processes leading to condensation and reevaporation. Determining this effective temperature of latent heat release is a fundamental question for understanding the thermodynamic behavior of moist convection.

Latent heat is an important part of the total heat transport due to moist convection. Hence, the expansion work of water vapor, diffusion of water vapor and irreversible phase changes play a significant role in the mechanical energy budget and the entropy budget of moist convection. Any investigation of these budgets

should therefore properly take these processes into consideration.

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APPENDIX

Relationships between Water Vapor Expansion and Water Vapor Transport

During its ascent in convective updrafts, water vapor expands and produces mechanical work. We derive here two relationships between water vapor transport and the expansion work performed by water vapor.

In section 2, the entropy variation associated with vapor pressure changes is defined as

$$\frac{W_{\text{vap}}}{T_{\text{vap}}} = - \int_{\Omega} \frac{\partial_t e + V_i \partial_i e}{T}. \quad (\text{A1})$$

The water vapor pressure e can be expressed as $e \approx (R_v/R_d)q_v p$, so that Eq. (A1) can be decomposed into a contribution due to changes in specific humidity and a contribution due to changes of total pressure:

$$\begin{aligned} \frac{W_{\text{vap}}}{T_{\text{vap}}} = & - \int_{\Omega} \frac{R_v p}{R_d T} (\partial_t q_v + V_i \partial_i q_v) \\ & - \int_{\Omega} \frac{R_v q_v}{R_d T} (\partial_t p + V_i \partial_i p). \end{aligned} \quad (\text{A2})$$

The first integral on the right-hand side of this equation can be rewritten using the perfect gas law $p \approx \rho R_d T$:

$$\begin{aligned} & - \int_{\Omega} \frac{R_v p}{R_d T} (\partial_t q_v + V_i \partial_i q_v) \\ & = -R_v \int_{\Omega} \rho (\partial_t q_v + V_i \partial_i q_v) \\ & = -R_v \partial_t \left(\int_{\Omega} \rho q_v \right) - R_v \int_{\Omega} \partial_i (\rho q_v V_i) = 0. \end{aligned} \quad (\text{A3})$$

The first term on the right-hand side is proportional to the change of the mass of water vapor. For a system in statistical equilibrium, this term vanishes. The second term on the right-hand side is proportional to the mass transport of water vapor through the lateral boundaries, and it also vanishes. Equation (A2) becomes

$$\frac{W_{\text{vap}}}{T_{\text{vap}}} = - \int_{\Omega} \frac{R_v q_v}{R_d T} (\partial_t p + V_i \partial_i p). \quad (\text{A4})$$

If the total pressure changes are dominated by the change due to vertical motion, as is often assumed in the construction of an anelastic model (Durran 1989), then the pressure variation can be approximated by $\partial_t p + V_i \partial_i p \approx w \partial_{\bar{p}} \approx -\bar{p} w g$. Equation (A4) becomes

$$\frac{W_{\text{vap}}}{T_{\text{vap}}} \approx \int_{\Omega} g \frac{R_v}{R_d T} \bar{\rho} w q_v = \frac{W_v}{T_v}. \quad (\text{A5})$$

Here, W_v is the contribution of water vapor to the buoyancy flux (see Pauluis et al. 2000):

$$W_v = \int_{\Omega} \bar{\rho} g w \frac{R_v}{R_d} q_v, \quad (\text{A6})$$

and the effective temperature of water vapor transport T_v is defined by

$$T_v = \left(\int_{\Omega} g \frac{R_v}{R_d T} \bar{\rho} w q_v \right)^{-1} W_v. \quad (\text{A7})$$

Equation (A5) indicates that the entropy change due to the change in water vapor pressure is related to the vertical transport of water vapor. This result is utilized in section 3. It does not, however, ensure that the expansion work of water vapor W_{vap} is related to W_v or that the effective temperature of water vapor pressure change T_{vap} is related to T_v . This question is addressed now, as it is relevant for the discussion in Part I of this study.

For an atmosphere in radiative–convective equilibrium, the expansion work can be obtained from the water vapor pressure change:

$$W_{\text{vap}} = \int_{\Omega} e \partial_i V_i = - \int_{\Omega} \partial_i e + V_i \partial_i e, \quad (\text{A8})$$

where the second equality results from the fact that both $\int_{\Omega} \partial_i e$ and $\int_{\Omega} \partial_i (V_i e)$ vanish for an atmosphere in radiative–convective equilibrium. Using the relationship $e \approx (R_v/R_d) q_v p$, this becomes

$$W_{\text{vap}} = - \int_{\Omega} \frac{R_v p}{R_d} (\partial_i q_v + V_i \partial_i q_v) - \int_{\Omega} \frac{R_v q_v}{R_d} (\partial_i p + V_i \partial_i p). \quad (\text{A9})$$

As in the previous section, pressure changes can be approximated by the changes due to vertical motion: $\partial_i p + V_i \partial_i p \approx w \partial_p \approx -\bar{\rho} g w$. This then yields

$$- \int_{\Omega} \frac{R_v q_v}{R_d} (\partial_i p + V_i \partial_i p) \approx \int_{\Omega} \frac{R_v}{R_d} \bar{\rho} g w q_v = W_v. \quad (\text{A10})$$

If h_c is the average height at which condensation occurs, then W_v can be approximated by

$$W_v \approx \frac{R_v}{R_d} g h_c P. \quad (\text{A11})$$

The first integral on the right-hand side of (A9) can be written as

$$\begin{aligned} W_1 &= - \int_{\Omega} \frac{R_v p}{R_d} (\partial_i q_v + V_i \partial_i q_v) \\ &= - \int_{\Omega} R_v \rho T (\partial_i q_v + V_i \partial_i q_v) \\ &= - \int_{\Omega} R_v T (E - C - \partial_i J_{v,i}), \end{aligned} \quad (\text{A12})$$

where we use the continuity equation of water vapor (6). If T_l is the average temperature at which condensation occurs,^{A1} then the first integral is approximately given by

$$W_1 \approx R_v (T_l - T_{\text{surf}}) P. \quad (\text{A13})$$

Hence, the ratio between the first and second integral in (A9) is

$$\frac{W_1}{W_v} \approx \frac{R_d (T_l - T_{\text{surf}})}{g h_c} = \frac{H_p}{H_T}, \quad (\text{A14})$$

where $H_p = -(\partial_z \ln p)^{-1} = g^{-1} R_d T$ is the pressure scale height and $H_T = h_c T (T_l - T_{\text{surf}})^{-1} \approx -(\partial_z \ln T)^{-1}$ is the temperature scale height. The expansion work performed by water vapor can thus be approximated by

$$W_{\text{vap}} \approx \left(1 - \frac{H_p}{H_T} \right) W_v. \quad (\text{A15})$$

The pressure scale height in the atmosphere is $H_p \approx 8$ km. The temperature scale height is $H_T \approx 50$ km for the tropical atmosphere. As the ratio H_p/H_T is small, the buoyancy flux due to water vapor transport W_v is a first order approximation of the expansion work due to water vapor.

Combining (A5) and (A15) also shows that the effective temperature of water vapor pressure change T_{vap} can also be approximated by the effective temperature of water vapor transport T_v :

$$T_{\text{vap}} \approx \left(1 - \frac{H_p}{H_T} \right) T_v. \quad (\text{A16})$$

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^{A1} Notice that this average temperature T_l is close but not equal to the effective temperature T_{lat} .