Supplementary Material to the Manuskript

Irreversible Thermodynamics of Seawater Evaporation

Review of Mass Transfer Coefficients Employed in the Dalton Equation

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[†] Dedicated to the 150th anniversary of the appearance of Gibbs' Fundamental Thermodynamic Relation.

Abstract: In the present document a compilation of empirical, semiempirical, and theoretical expressions for the water-vapor pressure and specific humidity-based mass transfer coefficients employed in the Dalton equation is presented.

1. Turbulence-induced vertical transport in the atmospheric surface layer

a. Empirical approach

Daily and monthly evaporation rates can be effectively parameterized in terms of routinously measured meteorological observables among which the wind velocity is the key aerodynamic driver for water-vapor mass transfer across the sea-atmosphere interface (next to the relative fugacity or its proxies as the thermodynamic driving force of evaporation) (e.g., Wüst 1920, Sverdrup 1936, Jacobs 1942, 1951, Sutton and Simpson 1934, Penman and Keen 1948, Tomczak 1939, Brogmus 1958, 1959, Budyko 1963, Dammann 1965, Sellers 1965, Richter 1969, 1977, 1978, 1997, Richter et al. 1979, Kunz 1972; Dyck and Peschke 1983, pp. 137–141; Vietinghoff 2000; DWA 2018, pp. 103-122, Table 15) [22, 23, 91-97, 27, 98, 26, 99-107]. The first trials to directly calculate the evaporation can be probably traced back to Dalton (1798) [2], who proposed the following simple relation:

$$X_E = f(U)\,\Delta e, \quad \Delta e = e_{eq}(S_A, T) - e\,. \tag{1}$$

Here, $X_E = \{E, J_E\}$ denotes the evaporation metrics, which can be either the evaporation velocity (or evaporation rate), E (in units of m s^{-1}), or the water-vapor mass flux density, J_E (in units of kg m^{-2} s^{-1}). The quantity Δe denotes the thermodynamic driving force of evaporation, given by the difference between the equilibrium water-vapor pressure, $e_{eq}(S_A, T)$, as a function of the salinity and temperature, and the actual water-vapor pressure, e. The aerodynamic prefactor $f(U)$ is a nonlinear function of the wind velocity, U, and is called "wind function". The unit of $f(U)$ depends on the choice of X_E. In the literature, Eq. (1) is frequently given in form of a tailored equation expressed in non-SI units. The aerodynamic prefactor is not a universal (generally valid) function of U, but depends on several factors, such as the local wind field, which is influenced by topography, orographic roughness, shore conditions (morphology, vegation, house building), location of the measurement site etc. This holds true especially for inland waters. Correspondingly, there are different types of wind functions. Already Tomczak (1939) [95] addressed the question, whether it is allowed to extrapolate the local water-vapor mass flux density, J_E, to the whole free water area, A_E, i.e., to determine the total evaporation mass flux from multiplication of the mass flux density with the free-water area, $F_E = J_E A_E$. The author denied the answer. Based on the evaporation theory of Sutton and Simpson (1934) [93], Tomczak (1939) [95] analyzed the influence of the fetch on the evaporation rate and derived an analytical expression for the wind function, which depends next to Uon the degree of turbulence, and on the geometrical dimensions of the free-water area. A further discussion of this problem can be found in Richter (1969) [99]. A consequence of this problem is that the validity of empirical relations is more or less restricted to the special conditions of their derivation. Hence, special care is required when extrapolating empirical relations from one place to another. Compilations and critical reviews of empirical and semiempirical correlations for the estimation of the evaporation of free water areas can be found, e. g., in Vietinghoff (2000, pp. 51–60) [106] and DWA (2018, p. 103-122, Table 15) [107].

b. Rationale of the Monin-Obukhov similarity theory

In contrast to empirical and semiempirical approaches for daily and monthly means, the determination of instantaneous evaporation fluxes, e.g., in model applications, requires the explicit consideration of the atmospheric stability, which controls the turbulence exchange of water vapor in the atmospheric surface layer (ASL). Such approach requires the completion of empirical findings by additional theoretical considerations.

The Monin-Obukhov similarity theory (MOST) serves as a master theory for the treatment of ASL turbulence. This theory was originally published in Russian in 1954, later translated and published in German and English languages (e.g., Monin and Obuchow 1958; Monin and Obukhov 1990) [108, 109]. A review of the history, assumptions, rationale, and predictive power of the MOST can be found in, e. g., Foken (2004) [110]. Owing to its widespread presence in atmospherically relevant literature, especially on atmospheric boundary layer (ABL) physics (e.g., PalArya 1988; Foken 1990; Schmugge and André 1991; Garratt 1992; Kaimal and Finnigan 1994; Stull 1997; Etling 2010; Foken 2016; Emeis 2022) [111-119], here one can abstain from a comprehensive review of referenced sources. The explanations given below will focus on the rationale of this theory.

The MOST is based on the following assumptions:
1. The application of the MOST is restricted to the ASL, the height of which is denoted as H.
2. The universal laws predicted by the MOST rely on similarity considerations, which are typically applied in aero-hydrodynamics and thermal physics.
3. The flow is assumed to be horizontally homogeneous and to be free of acceleration.
4. Vertical motions are neglected.
5. Turbulence is assumed to be in a quasi-steady state.
6. The turbulent fluxes of momentum and heat are assumed to be independent of height, i.e., the ASL is approximated as a "constant-flux layer".
7. In the system of equations describing the momentum, mass, and heat budgets of a thermally inhomogeneous medium, terms containing the viscosity and thermal conductivity of the fluid are neglected. Under the condition of fully developed turbulence these terms must only be considered in the description of the details of the microstructure of the wind and temperature field.
8. The differences between the temperature and the potential temperature in the ASL and their vertical gradients are negligibly small. However, in the vicinity of isothermal states, these differences become important and must be considered.

In its orginal form, the MOST is formulated for a dry ASL (Monin and Obuchow 1958) [108], but it is commonly agreed, that the rules for the heat flux can also be applied to specific humidity or any other passive tracer, hence the heat-flux relations are applicable to scalar fluxes. Under these conditions, the MOST describes the turbulence in a thermally inhomogeneous medium by only four independent observables (e. g., Foken and Richter 1991, p. 9 therein) [120], namely
1. the screening height z,

2. the buoyancy parameter $\beta_B = g/T$ with g denoting the gravitational acceleration, and T the temperature at the screenibng height,
3. the momentum flux $J_U = -|\tau_{xy}^2 + \tau_{yz}^2| = -\varrho_{AV} u_*^2$ (in units of N m-2), with τ_{xy} and τ_{yz} denoting the xy- and yz-components of the Reynolds stress tensor, ϱ_{AV} the mass density of humid air, and u_* the friction velocity, and finally
4. the sensible heat flux $J_T = \varrho_{AV} c_P \overline{(w'T')_s}$ (in units of W m-2), with c_P denoting the isobaric heat capacity of humid air, $\overline{(w'T')_s} = -u_* T_*$ the kinematic heat flux (in units of K m s-1), T_* the kinematic scaling temperature, $w = \overline{w} + w'$ the vertical velocity, and $T = \overline{T} + T'$ the temperature employing the Reynolds decomposition in a mean part (overbar) and a deviatoric part (apostroph).

These four quantities define a dimensionless stability parameter ζ,

$$\zeta = \frac{z}{L}, \quad L = -\frac{u_*^3}{\kappa\, \beta_B \overline{(w'T')_s}}, \tag{2}$$

with a characteristic turbulence length scale, L, serving as a key scaling length of the MOST, which found entrance in the literature as Monin-Obukhov length (MOL). The quantity κ is the Von Karman constant. The upper limit of the ASL height is estimated to amount

$$H \approx \alpha \times 250\ \text{m}, \qquad \frac{u_*^2(0) - u_*^2(H)}{u_*^2(0)} \leq \alpha,$$

where α is a prescribed parameter controlling the vertical gradient of the momentum flux (vanishing vertical gradient at $\alpha = 0$). For $\alpha = 0.2$ the ASL height amounts $H = 50$ m. The most important prediction of the MOST is the existence of similarity laws for the vertical gradients of the horizontal wind velocity, $U = |\vec{U}|$, $\vec{U} = u\vec{\imath} + v\vec{\jmath}$, the temperature, T, and the specific humidity, q:

$$\frac{\kappa\, z}{\chi_*}\frac{\partial \bar{\chi}}{\partial z} = \Phi_\chi(\zeta), \quad \bar{\chi} = \{\overline{U}, \overline{T}, \bar{q}\}, \quad \chi_* = \{u_*, T_*, q_*\}$$

$$\curvearrowright \quad \frac{\kappa\, z}{u_*}\frac{\partial \overline{U}}{\partial z} = \Phi_U(\zeta), \quad \frac{\kappa\, z}{T_*}\frac{\partial \overline{T}}{\partial z} = \Phi_T(\zeta), \quad \frac{\kappa\, z}{q_*}\frac{\partial \bar{q}}{\partial z} = \Phi_q(\zeta)\,. \tag{3}$$

The quantities $\Phi_U(\zeta)$, $\Phi_T(\zeta)$, and $\Phi_q(\zeta)$ are are universal similarity functions for momentum, heat, and humidity, which must be empirically determined. In the limiting case of neutral stratification one has $J_T = 0$, resulting in $L \to \infty$ and $\zeta = 0$. The restoration of the logarithmic wind profile under neutral conditions requires $\Phi_U(0) = 1$. The quantities u_*, T_*, and q_* are independent of altitude and serve as characteristic scaling properties. A direct consequence of the MOST is the mutual interdependence of momentum, heat, and evaporation fluxes.
Now it is assumed, that the validity of the relations given in Eq. (3) is restricted to turbulent layers of thicknesses $\Delta z|_U = z - z_0$, $\Delta z|_T = z - z_{0,T}$, and $\Delta z|_q = z - z_{0,q}$ for momentum, heat, and moisture transport, respectively. The quantities z_0, $z_{0,T}$, and $z_{0,q}$ are the aerodynamic roughness lengths for momentum, temperature, and specific humidity defining the lower height of the applicability of the MOST scaling laws. Adding a nutritive zero, 1-1=0, to the right-hand side of the first scaling relation in Eq. (3), the integration over the height from the aerodynamic roughness length z_0 to the screening height z delivers:

$$\Delta\overline{U} = \overline{U}(z) - \overline{U}(z_0) = \frac{u_*}{\kappa}\int_{z_0}^{z} \frac{\Phi_U(\zeta(z'))}{z'}\, \mathrm{d}z' = \frac{u_*}{\kappa}\left[\ln\frac{z}{z_0} + I\right],$$

$$I = \int_{z_0}^{z} \frac{\Phi_U(\zeta(z')) - 1}{z'}\, \mathrm{d}z' = -\left[\Psi_U(\zeta) - \int_0^{\zeta_0} \frac{1 - \Phi_U(\zeta')}{\zeta'}\, \mathrm{d}\zeta'\right],$$

$$\Psi_U(\zeta) = \int_0^{\zeta} \frac{1-\Phi_U(\zeta')}{\zeta'}\,\mathrm{d}\zeta'$$

$$\curvearrowright \quad \Delta\bar{U} = \frac{u_*}{\kappa}\left[\ln\frac{z}{z_0} - \Psi_U\left(\frac{z}{L}\right) + \Psi_U\left(\frac{z_0}{L}\right)\right]. \tag{4}$$

Analogously, carrying out the integration of the second relation in Eq. (3) from $z_{0,T}$ to z with $\bar{T}(z_{0,T}) = \bar{T}_s$ and of the third relation from $z_{0,q}$ to z with $\bar{q}(z_{0,q}) = \bar{q}_s$ one arrives at the following integrals:

$$\Delta\bar{T} = \bar{T}(z) - \bar{T}_s = \frac{T_*}{\kappa}\int_{z_{0,T}}^{z} \frac{\Phi_T(\zeta(z'))}{z'}\,\mathrm{d}z' = \frac{T_*}{\kappa}\left[\ln\frac{z}{z_{0,T}} - \Psi_T\left(\frac{z}{L}\right) + \Psi_T\left(\frac{z_{0,T}}{L}\right)\right],$$

$$\Psi_T(\zeta) = \int_0^{\zeta} \frac{1-\Phi_T(\zeta')}{\zeta'}\,\mathrm{d}\zeta', \tag{5}$$

$$\Delta\bar{q} = \bar{q}(z) - \bar{q}_s = \frac{q_*}{\kappa}\int_{z_{0,q}}^{z} \frac{\Phi_q(\zeta(z'))}{z'}\,\mathrm{d}z' = \frac{q_*}{\kappa}\left[\ln\frac{z}{z_{0,q}} - \Psi_q\left(\frac{z}{L}\right) + \Psi_q\left(\frac{z_{0,q}}{L}\right)\right],$$

$$\Psi_q(\zeta) = \int_0^{\zeta} \frac{1-\Phi_q(\zeta')}{\zeta'}\,\mathrm{d}\zeta'. \tag{6}$$

Considering $\Delta\bar{U}$, $\Delta\bar{T}$, and $\Delta\bar{q}$ as given, and inserting u_* from Eq. (4) together with T_* from Eq. (5) into Eq. (2), one obtains a transcendental equation for the determination of L, the knowledge of which allows the determination of u_*, T_*, and q_*:

$$u_* = \frac{\kappa\,\Delta\bar{U}}{\ln\frac{z}{z_0} - \Psi_U\left(\frac{z}{L}\right) + \Psi_U\left(\frac{z_0}{L}\right)}, \tag{7}$$

$$T_* = \frac{\kappa\,\Delta\bar{T}}{\ln\frac{z}{z_{0,T}} - \Psi_T\left(\frac{z}{L}\right) + \Psi_T\left(\frac{z_{0,T}}{L}\right)}, \tag{8}$$

$$q_* = \frac{\kappa\,\Delta\bar{q}}{\ln\frac{z}{z_{0,q}} - \Psi_q\left(\frac{z}{L}\right) + \Psi_q\left(\frac{z_{0,q}}{L}\right)}. \tag{9}$$

By virtue of $J_U = -\varrho_{AV} u_*^2$, $J_T = -\varrho_{AV} c_P u_* T_*$, and analogously, $J_q = -\varrho_{AV} L_V u_* q_*$, with L_V denoting the specific heat of evaporation, one arrives at the following flux representations for the turbulent transfer of momentum, sensible heat, and latent heat:

$$J_U = -\varrho_{AV} C_U [\Delta\bar{U}]^2, \quad C_U = \frac{\kappa^2}{\ln\frac{z}{z_0} - \Psi_U\left(\frac{z}{L}\right) + \Psi_U\left(\frac{z_0}{L}\right)}, \tag{10}$$

$$J_T = -\varrho_{AV} c_P C_T \Delta\bar{U}\Delta\bar{T}, \quad C_T = \frac{\kappa^2}{\left[\ln\frac{z}{z_0} - \Psi_U\left(\frac{z}{L}\right) + \Psi_U\left(\frac{z_0}{L}\right)\right]\left[\ln\frac{z}{z_{0,T}} - \Psi_T\left(\frac{z}{L}\right) + \Psi_T\left(\frac{z_{0,T}}{L}\right)\right]}, \tag{11}$$

$$J_q = -\varrho_{AV} L_V C_q \Delta\bar{U}\Delta\bar{q}, \quad C_q = \frac{\kappa^2}{\left[\ln\frac{z}{z_0} - \Psi_U\left(\frac{z}{L}\right) + \Psi_U\left(\frac{z_0}{L}\right)\right]\left[\ln\frac{z}{z_{0,q}} - \Psi_q\left(\frac{z}{L}\right) + \Psi_q\left(\frac{z_{0,q}}{L}\right)\right]}. \tag{12}$$

Here, C_U, C_T, and C_q denote the drag coefficient, the Stanton and the Dalton number, respectively. The application of Eqs. (10), (11), and (12) requires the specification of the similarity functions, $\Phi_\chi(\zeta)$, and the boundary conditions at z_0, $z_{0,T}$, and $z_{0,q}$. The availability of the Dalton number, C_q, allows a unique determination of the vapor-pressure and specific humidity-based transfer coefficients, D_e and $D_q = C_q\Delta\bar{U}$, appearing in the Dalton equation.

c. Applicational aspects and compilation of transfer coefficients

The MOST serves as the theoretical fundament of countless meteorological and metrological applications in parameterizing and measuring near-surface turbulent fluxes. For example, the MOST is part of the flux parameterization in several community models for numerical weather prediction (NWP) and global circulation models (GCM), such as,

- the NWP model COSMO of the German Weather Service (e. g., Doms et al. 2013) [121],
- the Integrated Forecast System (IFS) of the European Center for Medium-Range Weather Forecasts (ECMWF) (e. g., ECMWF-IFS 2021, https://www.ecmwf.int/en/publications/ifs-documentation) [122],
- the NCAR-GCM (e. g., Large and Pond 1981, 1982, Large et al. 1997, Large and Yeager 2004, 2009, Brodeau et al. 2017) [123-128], and
- the TOGA-COARE-GCM (e. g., Webster and Lukas 1992, Fairall et al. 1996a, b, 1997, 2003a, b, 2011, Andreas 2003, Andreas et al. 2008; Brunke et al. 2003; Zeng et al. 2003; Edson et al. 2013; Yusup et al. 2018) [129-141].

While retaining the basic physical assumptions of the theory, the specific implementation is subject to manifold modifications and enhancement to continuously ensure best agreement with available state-of-the-art empirical and theoretical findings and to remove still existing biases in the flux parameterization (e.g., Yu 2019) [142]. The variety of specifications concerns, e.g.,

- the specification of the empirical similiarity functions, $\Phi_\chi(\zeta)$, underlying the determination of the stability functions, $\Psi_\chi(\zeta)$, and the drag coefficient and the Stanton and Dalton numbers (e. g., Dyer and Hicks 1970, Dyer 1974, Paulson 1970; Businger et al. 1971; Kaimal et al. 1971, 1976, Skeib 1980; Foken and Skeib 1983; Skeib and Richter 1984; Holtslag 1987; Högström 1988; Foken 1990, 1991; Garratt 1992; Kaimal and Finnigan 1994; Fairall et al. 1996b; ECMWF-IFS 2021) [143-153, 112, 154, 114, 115, 131, 122],
- the parameterization of the surface-roughness lengths, at z_0, $z_{0,T}$, and $z_{0,q}$ (e. g., Smith 1988, Miller et al. 1992, Beljaars 1995, Fairall et al. 1996a,b, 1997, 2003a, 2011; Large and Yeager 2009; Doms et al. 2013; Edson et al. 2013; Liu et al. 2013) [155-157, 130-133, 135, 127, 121, 140, 158], and
- the refinement of the description of the exchange processes in the molecular boundary layer and the viscous intermediate (buffer) layer, i. e., at $0 \leq z \leq \{z_0, z_{0,T}, z_{0,q}\}$ (e. g., Owen and Thomson 1963, Kondo 1975, Foken et al. 1978, Liu et al. 1979, Foken 1979a, b, 1984, 1986; Foken and Richter 1991; Richter and Skeib 1991) [159, 160, 20, 161-165, 120, 166], e.g., within the framework of the surface-renewal theory (e. g., Brutsaert 1975; Soloviev and Schlüssel 1994, 1998; Clayson et al. 1996; Fairall et al. 1996a; Zappa et al. 1998; Mengistu and Savage 2010; Horvath and Chatterjee 2018; Hu et al. 2018) [167-170, 130, 171-174].

Table S1 contains a compilation of selected empirical and semi-empirical expressions of the vapor pressure and specific humidity-based transfer coefficients, D_e and D_q, appearing in the Dalton equation.