

Lecture 16, Water, Humidity, Pressure and Trace Gases, Part 1

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Topics to be covered:

1. Physical and chemical properties of water
2. Chemical Potential of Water
3. Gas Laws
 - absolute humidity
 - relative humidity
 - virtual temperature
 - Saturation Vapor Pressure
 - Clausius-Clapyeron Equation
4. Rainfall/Drought.

L16.1 Introduction

Water, in liquid and vapor forms, plays many roles in plant biology. With respect to plant physiology, its foremost function is in hydrating tissue, aiding cell expansion and growth and being a medium for the transfer of nutrients from the soil, through the roots and to the leaves and fruits.

How well a leaf is hydrated affects stomatal mechanics directly and indirectly. The turgidity of guard cells is what causes stomata to open. Indirect stomatal responses are triggered by hormonal signals, ABA, which are released when the soil dries, atmospheric humidity deficits and transpiration rates. In turn, how open or closed the stomata are affect transpiration, leaf temperature, the uptake of pollutants and the soil water budget. In regards to biochemistry, water is an active participant in photosynthetic reactions.

In the atmosphere, water exists as a vapor, liquid (rain, dew, fog, clouds) and solid (snow, frost). Atmospheric humidity sets the driving potential for canopy transpiration and soil evaporation. At saturation, suspended droplets form, causing fog and clouds. Clouds are highly reflective and diminish the radiation balance at the earth surface. Aerosols are more included to form when humidity is high. Water plays a role in the formation of OH, the hydroxyl radical, the atmosphere's vacuum cleaner, and hence the atmospheric

composition of the atmosphere. Water vapor is one of the most effective greenhouse gases, too.

Biometeorologists, plant pathologists and entomologists are interested in humidity because it facilitates the hatching of microbial spores and insect and spider eggs.

Atmospheric humidity is governed by biospheric sources and sinks and advection. **Sources** of humidity include **evaporation, transpiration, and sublimation**. **Losses** of atmospheric humidity occur by **precipitation, snow, dew and frost**. Advection occurs when humid or dry air masses move over a region or by the entrainment of dry air from the troposphere into the planetary boundary layer. Ultimately, water is continuously cycled on earth, between fresh and salt water reservoirs. Precipitation over land either evaporates, runs-off into lakes and rivers or is stored in the soil, glaciers and groundwater. Water that condenses into clouds can eventually return to the land when the clouds rain. The study of this cycling is formally within the domain of hydrology, but biometeorologist work actively in this area through their research on evaporation.

L16.2. Physical Properties of Water

Water is the main constituent of most plant cells. It can constitute up to 95% of lettuce and less than 5% of dry seeds. Water is of further importance for it is the medium by which the diffusion of solutes in cells and the soil take place.

Water, H₂O, has a molecular weight of 18 g mole⁻¹. Its melting point is 0 °C. Its boiling point is 100 °C. It is densest at 4 °C. It is incompressible. Its latent heat of vaporization is 2442 J g⁻¹ (at 25 C). On a mass basis, water has one of the highest rates of evaporation of any liquid. The specific heat of water is 1 calorie per gram at 14.5 C or using the preferred S.I. units 4.184 J g⁻¹.

Table 1 Summary of the properties of water

Property	Value
molecular weight	18 g mole ⁻¹
melting point	273.15 K
boiling point	373.15 K
latent heat of vaporization	2.442 MJ kg ⁻¹ or 44.00 kJ mol ⁻¹ at 20 C
latent heat of sublimation	2.826 MJ kg ⁻¹ or 51.00 kJ mol ⁻¹ at 0 C
dielectric constant	80
thermal conductivity	0.599 W m ⁻¹ at 20 C
heat capacity of water	4182 J kg ⁻¹ at 20 C
molecular diffusivity, water in air	2.42 10 ⁻⁵ m ² s ⁻¹ at 20 C
Density	1.000 kg m ⁻³ at 4 C

The arrangement of the water molecule is unique, compared to other low weight compounds (e.g. CO₂, CH₄). The atoms H-O-H are not arranged in a straight line.(180 degrees). Instead, they form an angle of 105 degrees, forming a polar molecule.

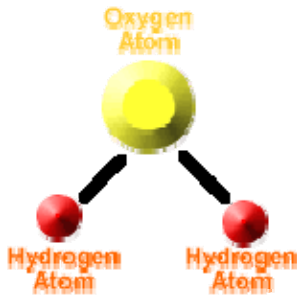


Figure 1 source www.princeton.edu/~chm112/project/water%20molecule.gif

The hydrogen atoms approximate naked protons on the surface of the oxygen atom. The net charge is zero, but the arrangement of atoms form a slightly positive charge on one side of the molecule and a negative one on the other side. This arrangement allows hydrogen bonding. It enables water to remain liquid at room temperature and minimizes vaporization. This is an exception for low weighted molecules. Consequently, water is a very effective solvent, due to its small molecular size, its polar characteristic and its high dielectric (80) constant. The high dielectric constant of water is a property that is exploited when measuring soil moisture with a time domain reflectometer.

Table 2 Temperature dependent properties of water (Campbell, Norman, 1998)

temperature	density	latent heat of evaporation	kinematic viscosity
°C	Mg m ⁻³	kJ mol ⁻¹	mm ² s ⁻¹
0	0.99987	45.0	1.79
4	1.0000	44.8	1.57
10	0.99973	44.6	1.31
20	0.99823	44.1	1.01
30	0.99568	43.7	0.80
40	0.99225	42.8	0.66

L16.3 Chemical Potential of Water

From everyday experience we know that water moves from regions of high to low elevations, as observed by watching a water fall, or the pure to salty regions as fresh dilutes sea water as it crosses a hydraulic barrier.

The concept of **chemical potential** quantifies the driving force for movement of water between two locations. The concept can also be used to determine whether a substance will undergo a chemical reaction. The chemical potential has units of energy (J mol^{-1}). The chemical potential of a chemical species is a function of its concentration, the pressure of the system, electrical potential and gravity (Nobel, 1999).

The **potential energy** of water is related to the difference between its chemical potential (μ_w) and a reference state (μ_w^o):

$$\psi = \frac{\mu_w - \mu_w^o}{V_w}$$

where V_w is the partial molal volume of water ($18.05 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}$). The chemical potential of water is related to the amount of change in the Gibbs free energy of the system, relative to changes in water content, as pressure, temperature and minor constituents, e.g., salts, n_x , remain constant.

$$\mu_w = \left. \frac{\partial G}{\partial n_w} \right| T, P, n_x$$

(incremental changes in Gibbs free energy is defined as: $dG = -SdT + VdP + \sum_{i=1} \mu_i dn_i$)

Water potential has units of pressure ($\text{F/A} \sim \text{kg m s}^{-2} \text{ m}^{-2}$) rather than that of work ($\text{F} \times \sim \text{kg m s}^{-2} \text{ m}$) because it is expressed on a unit mass or volume basis, and the mass of water substituted for distance cubed, ($\text{kg m}^{-1} \text{ s}^{-2}$).

The **total water potential** of a system consists of the sum of water potentials associated with **pressure, osmotic, matrix** and **gravitational** forces:

$$\psi = \psi_p + \psi_\pi + \psi_m + \psi_g$$

The electrical potential is not considered for water, for it has no net charge.

The **pressure potential** is related to the hydrostatic pressure, as when someone is blow on or sucking on straw that is inserted in a reservoir of water. Its sign can be positive or negative.

The presence of solutes reduces the activity of water. This effect is measured by the **osmotic potential**.

$$\psi_{\pi} = \frac{RT}{V_w} \ln a_w$$

where R is the universal gas constant, T is temperature and a_w is the chemical activity. The activity of water is related to its mole fraction by:

$$\chi_w = \frac{a_w}{\gamma_w}$$

γ_w is an activity coefficient and is equals to one in solutions that are very dilute.

The **matric potential** is non-zero when for water is diffusing through porous medium like soils. In this case, interactions between water and solid surfaces act to reduce the activity of water.

Gravity imposes a force on standing water. The gravitational force is a function of the density of water, the acceleration due to gravity and the height of the water reservoir above or below a reference height:

$$\psi_g = \rho_w g h$$

Its sign is positive if it is above the reference level, and is negative if vice versa. The gravitational potential is small for a short plant, but it can reach 0.5 MPa at the top of a 50 m redwood tree.

With many cases the water potential in the natural environment, as that of a soil or within the xylem of a plant, is less than zero.

L16.4 Gas Laws

The atmosphere consists of a mixture of gases. The predominant gases are nitrogen, oxygen, argon. Trace gases include water vapor, carbon dioxide, nitrous oxide, methane, ozone, NO_x, VOC and SO₂.

Table 3 Composition of air

constituent	percent by volume	percent by mass	molecular weight (g mole ⁻¹)
N ₂	78.091	75.5	28.02
O ₂	20.95	23.1	32.00
Ar	0.930	1.3	39.94
CO ₂	0.036	0.05	44.01

To understand the composition of the atmosphere, we start with the gas laws and some basic definitions of gaseous concentration. The ideal gas law, a relation that is derived from Charles Law and Boyle's Law, shows that pressure, volume and temperature are inter-related.

$$PV = nRT$$

where R is the universal gas constant, $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$, T is absolute temperature (K), P is pressure (Pa, N m^{-2}), V is volume and n is the number of moles.

An alternate expression is:

$$P\alpha = \frac{RT}{m} = \frac{\rho RT}{m}$$

where m is the molecular weight of a gas (g mol^{-1}), ρ is the mass density (g m^{-3}) and α is $1/\rho$.

Increasing temperature of a confined volume increases the kinetic energy of gas molecules. Their increased motion can bounce harder on the sides of the container and increase its pressure. Adding more material into a container also increases its pressure. On the other hand, expanding the volume of an isothermal gas will decrease its pressure.

The pressure of air is the sum of partial pressures of constituent gases:

$$P = p_{N_2} + p_{O_2} + p_{Ar} + p_{CO_2} + p_{H_2O} \dots$$

At sea level the atmospheric pressure is: 0.1013 MPa, 101.3 kPa or 1013 mb

From the gas law we can compute the molar volume of air (volume occupied by one mole of air, $n=1$) for standard pressure (0.1013 MPa, 101.3 kPa, 1013 mb) and temperature (273.15 K),

$$V = \frac{RT}{P}$$

which equals $22.41 \text{ liters mole}^{-1}$ or $0.02241 \text{ m}^3 \text{ mol}^{-1}$.

We calculate the density of air using

$$\rho = \frac{Pm}{RT}$$

The molecular mass of dry air is $28.964 \text{ g mole}^{-1}$.

Table 4 **Density of Air at 100.0 kPa**

T	dry	Saturated
°C	Kg m ⁻³	kg m ⁻³
0	1.292	1.289
5	1.269	1.265
10	1.246	1.240
15	1.225	1.217
20	1.204	1.194
25	1.183	1.169
30	1.164	1.145
40	1.128	1.096

We are familiar with the term concentration from reading the newspaper about the CO₂ record at Mauna Loa. However, there are four terms that we need to consider when studying the composition of the atmosphere. These terms arise by how they are measured or normalized. These terms are derived from either a molar and mass basis.

1. **mass gas density** (grams of a gas molecule per unit volume)

$$\rho_c = \frac{n_c m_c}{V} = \frac{p_c m_c}{RT}$$

n_c is the number of moles, V is volume and m_c is the molecular mass (g mole⁻¹) of the compound.

2. **molar gas density** (moles of a gas molecule per unit volume)

$$c = \frac{n_c}{V} = \frac{p_c}{RT} = \frac{\rho_c}{m_c}$$

3. **Mass fraction** (mass per unit mass of air)

$$M_c = \frac{\rho_c}{\rho_a} = \frac{\chi_c m_c}{m_a}$$

4. **Mole fraction**, the number of moles of a trace gas divided by the total number of moles present in the mixture

$$\chi_c = \frac{\sum n_c}{n}$$

Dalton's Law of partial pressure states that the total pressure is the sum of the partial pressures of the constituents of the mixture

$$C_c = \frac{n_c}{n_a} = \frac{m_a \rho_c}{m_c \rho_a} = \frac{p_c}{p_a}$$

The mole fraction can also be described on the basis of dry air, rather than moist air. In this situation C is defined as:

$$C_c = \frac{n_c}{n_d} = \frac{p_c}{p_d} = \frac{p_c}{p_a - p_{H_2O}}$$

a. Water Vapor

Relative Humidity, h_r , is the ratio between the actual and saturation vapor pressures. It ranges between zero and 1.0, with one indicating saturation.

$$h_r = \frac{e_a}{e_s(T)}$$

The relative humidity varies widely over the course of a day or year. Measurements of temperature need to accompany measurements of RH to assess the actual humidity and other measures.

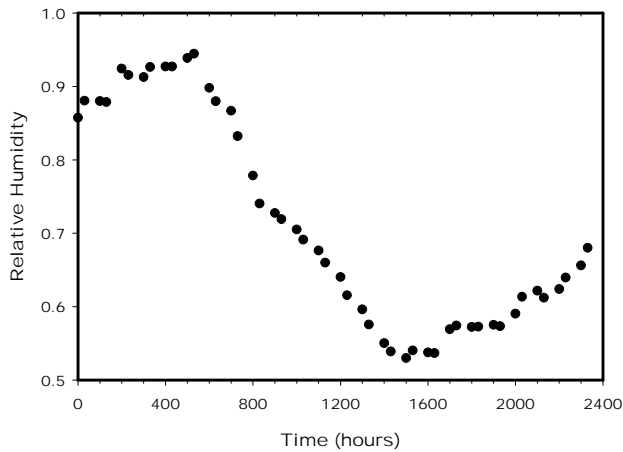


Figure 2 Diurnal course of relative humidity over a deciduous forest

Absolute humidity or vapor density (g m^{-3}):

$$\rho_v = \frac{e_a m_v}{RT_k}$$

($R=8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$ $m_v=18 \text{ g mol}^{-1}$)

$$\rho_v(\text{g} \cdot \text{m}^{-3}) = \frac{2.165 \cdot e_a(\text{Pa})}{T_k}$$

$$\rho_v(\text{g} \cdot \text{m}^{-3}) = \frac{2165 \cdot e_a(\text{kPa})}{T_k}$$

We can also explore how absolute humidity varies with constant e , $e_s(T)$ and relative humidity.

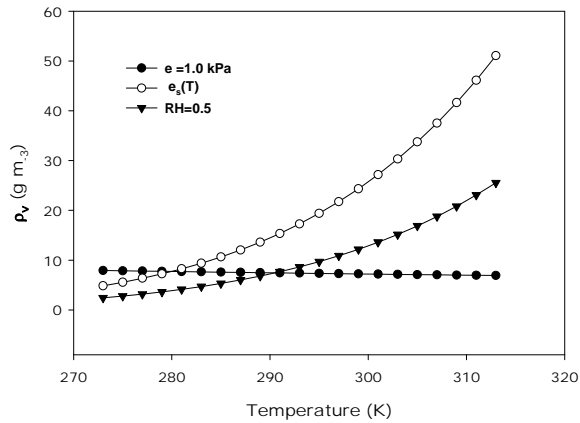


Figure 3 Variation in absolute humidity with temperature

Over the course of a day absolute humidity over an actively transpiring, irrigated crop may vary by 2 g m^{-3} .

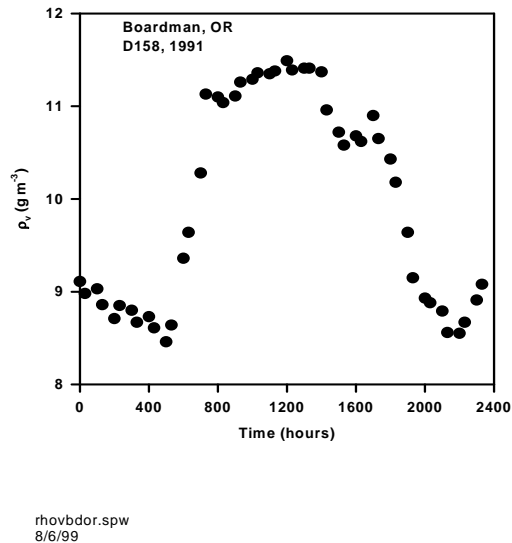


Figure 4 Diurnal pattern of absolute humidity over an evaporating crop

The **specific humidity** is the mass of water vapor per unit mass of moist air (g kg^{-1}):

$$m = \frac{\rho_v}{\rho} = \frac{m_v e}{m p}$$

Mixing Ratio or Mole Fraction

$$\chi = \frac{e_a}{p}, \text{ with respect to moist air}$$

$$\chi_d = \frac{e_a}{p - e_a}, \text{ with respect to dry air}$$

b. Virtual temperature

In meteorology we are interested in buoyancy, which can arise from density differences due to temperature or gas composition (dry vs moist air) (Wallace, Hobbs, 1977). It is convenient to define a fictitious temperature, **virtual temperature**. It is the temperature **dry air would have if it had the same density as moist air at the same pressure**.

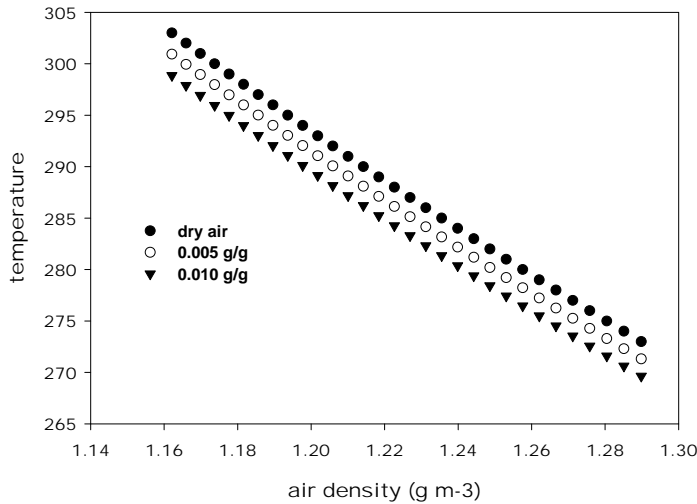


Figure 5 Relation between air density, humidity and temperature

It ends up being more convenient to use virtual temperature as often does not know the weighted molecular mass the moist air mixture, but one does know the molecular mass of dry air, m_a .

$$P = (P - e)|_{dry} + e|_{moist} = \frac{\rho RT}{m} = RT \left(\frac{\rho_a}{m_a} + \frac{\rho_v}{m_v} \right) = \frac{\rho RT_v}{m_a}$$

$$\frac{\rho}{m} = \left(\frac{\rho_a}{m_a} + \frac{\rho_v}{m_v} \right)$$

$$\frac{1}{m} = \frac{1}{M_a + M_v} \left(\frac{M_a}{m_a} + \frac{M_v}{m_v} \right)$$

capitals represent mass of dry air and vapor, lower case is the molecular weights (g per mole). Algebraic manipulations leads to:

$$\frac{1}{m} = \frac{M_a}{(M_a + M_v)m_a} \left(1 + \frac{m_a M_v}{m_v M_a}\right)$$

$$\frac{M_v}{M_a} = \frac{\rho_v}{\rho_a}$$

$$\frac{P}{\rho} = \frac{R}{m_a} \left\{ T \frac{1 + \frac{m_a \rho_v}{m_v \rho_a}}{1 + \frac{\rho_v}{\rho_a}} \right\} = \frac{R}{m_a} T_v$$

$$T_v = T \left(\frac{1 + \frac{m_a \rho_v}{m_v \rho_a}}{1 + \frac{\rho_v}{\rho_a}} \right)$$

$$T_v = T \left(1 + 0.38 \frac{e}{P} \right)$$

Why are we interested in this fictitious virtual temperature? We are interested in virtual temperature, for it is related to the **speed of sound** and the **buoyancy of the air**.

Knowledge of the speed of sound is used by sonic anemometers to measure directional wind velocity and temperature.

$$v_{sound} = \sqrt{\frac{C_p P}{C_v \rho}} = \sqrt{\frac{C_p RT_v}{C_v m_{air}}}$$

Buoyancy of air is caused by density differences. And buoyancy produces turbulence. Warm is less dense than dry air at a reference temperature, as is moist air compare to dry air.

Acceleration of a parcel of air due to buoyancy is

$$a = g \frac{(\rho - \rho_{parcel})}{\rho_{parcel}}$$

From the gas laws relative fluctuations in density are related to temperature fluctuations

$$\text{For dry air: } \frac{\rho_a'}{\rho_a} = \frac{T'}{T}$$

$$\text{For moist air: } \frac{\rho'}{\rho} = \frac{T'}{T_v}$$

so

$$a = -g \frac{(T_v - T_{vp})}{T_v}$$

c. Saturation Vapor Pressure

When a pool of water is at constant temperature in a closed container, some water molecules are leaving the liquid and others are condensing and returning to the liquid. Molecules in the head space exert a partial pressure on the system. The equilibrium vapor pressure that occurs is called the saturation vapor pressure. It is a function of temperature and is independent of pressure.

Clausius-Clapeyron Equation is used to quantify the saturation vapor pressure-temperature curve (Wallace, Hobbs, 1977). It is also used to derive other moisture quantities such as absolute and relative humidity, saturation vapor pressure, dew point.

Clapeyron derived the relation between how vapor pressure changes with respect to a change in temperature, dP/dT . If two phases of a pure substance (such as the liquid and vapor phases of water) are in equilibrium with each other then they have the same Gibbs energy at that temperature and pressure. If the temperature and pressure of both phases are changed in such a manner that the chemical potentials of each phase is equal to one another, the change in entropy and enthalpy with respect to change in volume, then both phases can co-exist.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

Clausius simplified the Clapeyron equation to define a relation for vapor pressures at different temperatures

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vapor}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{\Delta H_{vapor} (T_2 - T_1)}{R \cdot T_1 \cdot T_2}$$

Derivation come by manipulating dP/dT and substituting RT/P for V .

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vapor}}}{TV_{\text{vapor}}} = \frac{P\Delta H_{\text{vapor}}}{RT^2}$$

The enthalpy of vaporization for a liquid we can be assessed for the molar entropy of vaporization at a standard boiling point, such as one atmosphere, which is constant for most liquids ($21 \text{ C K}^{-1} \text{ mol}^{-1}$). Thereby,

$$\Delta S_{\text{vapor}} = \frac{\Delta H_{\text{vapor}}}{T_{\text{boiling}}}$$

One is also able to calculate changes in the saturation vapor pressure of water vapor as a function of the latent heat of phase change (L_x) and the inverse of Temperature and the change is specific volume (1/density).

$$\frac{de_s}{dT} = \frac{L_x}{T(\alpha_2 - \alpha_1)}$$

Various functions have been developed to compute the saturation vapor pressure (Campbell, Norman, 1998; Wallace, Hobbs, 1977). With temperature in terms of degrees Celsius one can use:

$$e_s(T_C) = 0.611 \exp\left(\frac{17.502 \cdot T_C}{T_C + 240.97}\right)$$

The exponential nature of $e_s(T)$ has many implications on leaf energy balance, leaf temperature, transpiration and respiration. The leaf, within the stomatal cavity, is assumed to be saturated. A 10 degree increase in leaf temperature can double cause a geometric increase in the air surface humidity difference and increase dramatically the potential for evaporation. As a general rule of thumb the saturation vapor pressure, e_s equals 611 Pa at 0 °C and approximately doubles for each 10 °C increase in temperature.

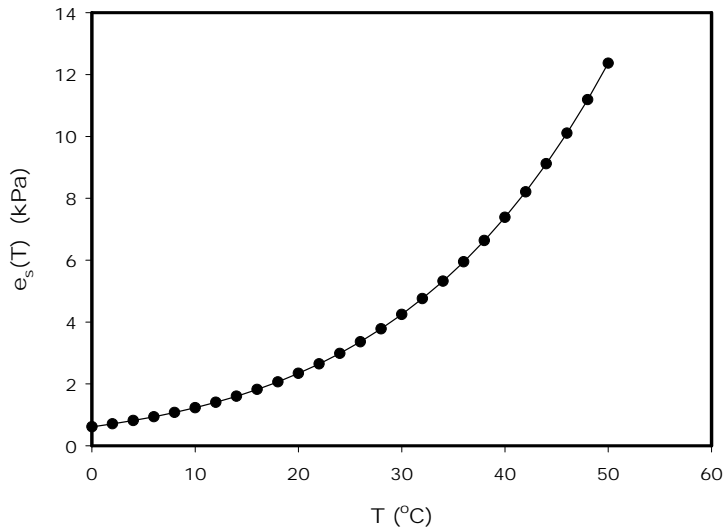


Figure 6 Saturation vapor pressure vs temperature curve

An empirical function for saturation vapor pressure, in terms of degrees Kelvin, is:

$$e_s(T_k) = 0.1 \cdot \exp\left(54.878 - \frac{6790.49}{T_k} - 5.02808 \ln(T_k)\right)$$

Alternatively, a fourth order empirical equation can be used for computing e_s (Paw U, Gao, 1988):

$$e_s(T) = 617.4 + 42.22 T + 1.675 T^2 + 0.01408 T^3 + 0.0005818 T^4, \text{ where } T \text{ in } ^\circ\text{C}, e_s \text{ (Pa)}.$$

An example of the diurnal variation in e_a and e_s is given below.

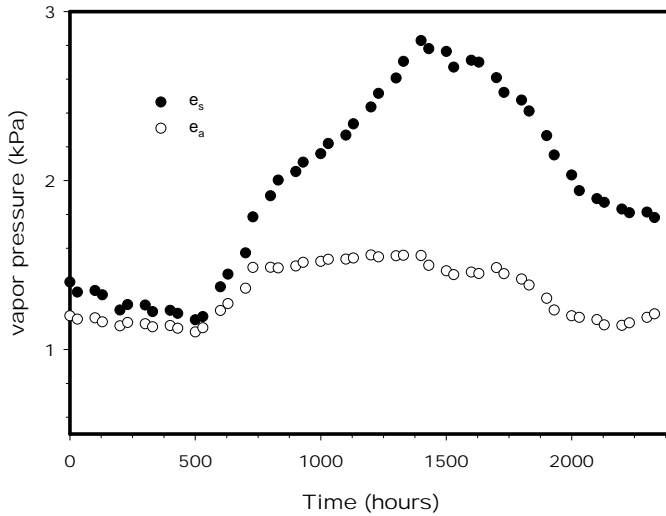


Figure 7 Diurnal pattern of vapor pressure and saturation vapor pressure.

The daily amplitude is much greater for e_s , as compared to e_a , because e_s is strongly coupled to the daily temperature change. The magnitude of the diurnal change in e_a is buffered by the growth of the planetary boundary layer, even when the underlying biosphere is evaporating. A growing boundary layer entrains dry air from above.

Rainfall Statistics

Whether a rain event occurs or not is a discrete Poisson process, whether it rains or not is independent of prior history. Ecohydrologists use probability statistics to define the time between storms and the size of each storm (Rodriguez-Iturbe, 2000). The probability of time between storms is

$$f(\tau) = \lambda \exp(-\lambda\tau)$$

λ is the rate of rain (units of rain events per day). It is computed by summing the number of rain days per year and dividing by 365. The inverse ($1/\lambda$) is the mean number of days between storm events. The amount of rain that falls, h , has a probabilistic distribution that is defined by the mean depth of rain per storm

$$f(h) = \frac{1}{\alpha} \exp\left(-\frac{h}{\alpha}\right)$$

$1/\alpha$ is the depth of the rain. α is computed by summing the amount of rain per year and dividing by the number of rainy days.

As noted by the definitions, the parameters for these two equations can be determined from climatology.

Rainfall statistics are important sources of information for predicting long term effects of rain variability on ecology and hydrology.

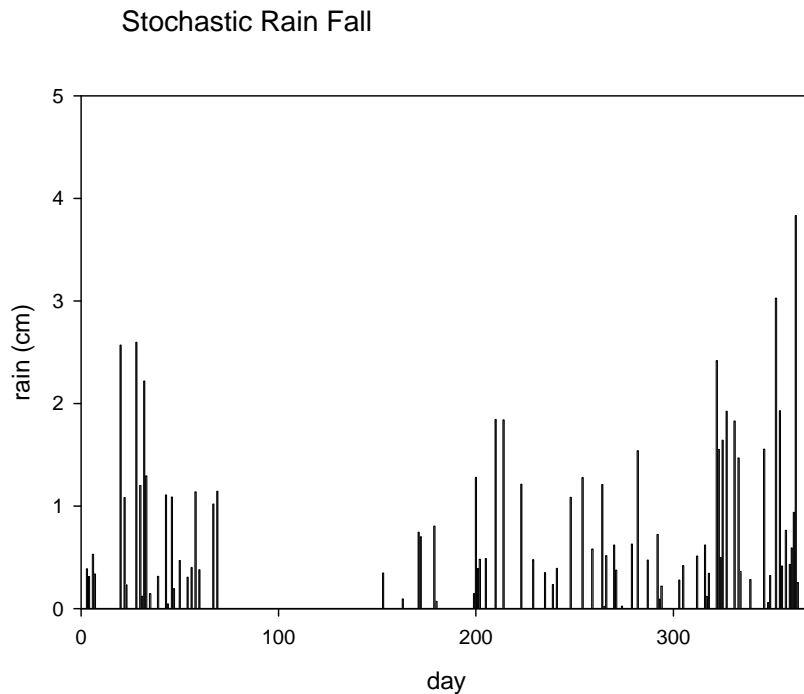


Figure 8 Example of synthetic rainfall for Ione California.

Summary points

- The concept of chemical potential energy quantifies the driving force for movement of water between two locations, such as in the soil, in a plant and between the soil, plant and atmosphere.
- Matrix, pressure, osmotic, gravitational potential sum to determine the chemical potential of water.
- Saturation vapor pressure is an exponential function of temperature
- The probability of rainfall events and its amount can be computed with a Poisson probability distribution

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