Lecture 14, Water, Humidity, Pressure and Trace Gases, Part 1

- Physical and chemical properties of water
- Gas Laws
- Chemical Potential of Water
- Rainfall/Drought

Atmospheric Gas Composition

constitue nt	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
H2O	?		18

Biometeorology, ESPM 129

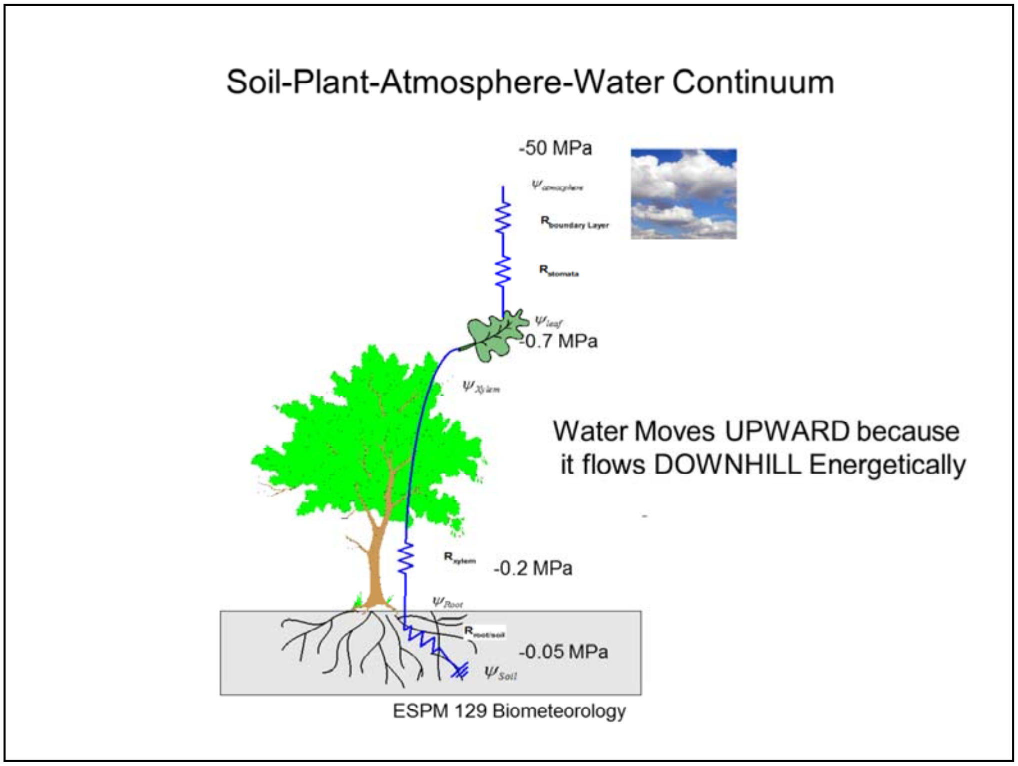
The atmosphere is comprised of gases. What are these gases and what is their proportion? Humidity is variable and can range from 1 to 4%

Water

- Gas
- Liquid
- Solid

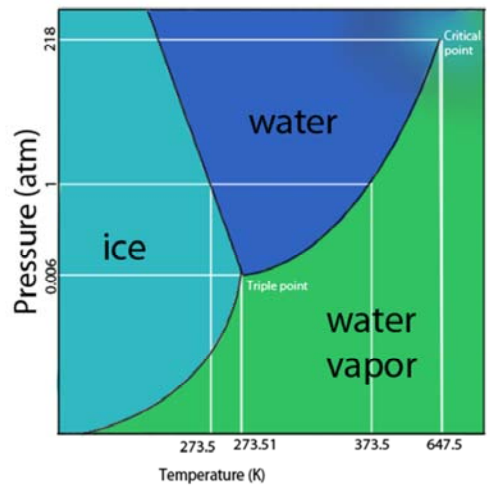
Biometeorology, ESPM 129

Water exists in 3 states



The transfer of water is important for biometeorology. We define the soil-plant-water continuum and use resistance models to conceptualize the transfer. The gradients of water are most effective when described in terms of energy, eg water potential. Here you can see water may move uphill physically, but it always moves downhill energetically.

Triple Point for Water

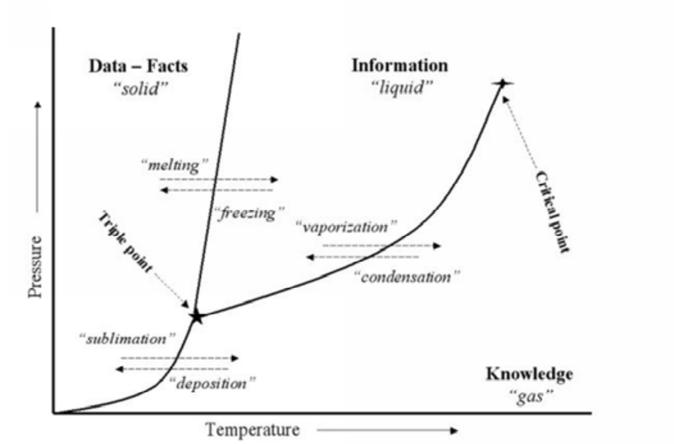


http://chemwiki.ucdavis.edu/@api/deki/files/7399/=f_copy.png

Biometeorology, ESPM 129

There is a critical temperature where water can exist in 3 phases.

Phase Changes of Water

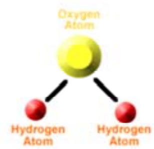


How can we Exploit the Triple Point Curve to prevent water from condensing on our air sampling tube?

http://www.laetusinpraesens.org/musings/images/climate_files/phase1.jpg

Biometeorology, ESPM 129

If we sample water through a tube, it can often condense on the walls. This will alter the water content delivered to a sensor. Sucking air through a tube can reduce its pressure and reduce its vulnerability to condense on walls.



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-1at 0 C
dialectric 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

Biometeorology, ESPM 129

General knowledge. Some physical properties of water

Properties of Water, f(T)

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

Measures of Atmospheric Moisture

- Water Potential, Pa
- Relative Humidity, unitless
- Dew Point Temperature, C
- Wet Bulb Temperature, C
- Vapor Pressure, Pa
- Vapor Pressure Deficit, Pa
- Density, mole m^{-3}
- Mixing Ratio, unitless

Biometeorology, ESPM 129

Measures of moisture

Charles Law and Boyle's Law

pressure, volume and temperature are inter-related.

$$PV = nRT$$

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

Biometeorology, ESPM 129

Let's explore moisture in the atmosphere starting with gas laws.

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),

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

22.41 liters $mole^{-1}$ or 0.02241 m^3 mol^{-1}.

Gas Law used by Meteorologists

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

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

Biometeorology, ESPM 129

Partial Pressure Law

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

$$p = \frac{R}{m} \rho T$$

$$\frac{\rho_a}{m_a} + \frac{\rho_v}{m_v} + \frac{\rho_c}{m_c} + \ldots = \frac{p}{RT}$$

Biometeorology, ESPM 129

Partial pressure law

Air Density

$$\rho = \frac{(P-e)m_a}{RT} + \frac{e\,m_v}{RT}$$

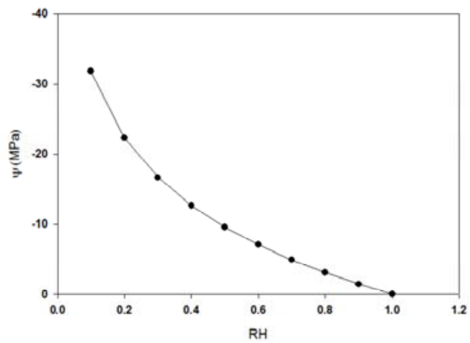
T	dry	Saturated
^oC	Kg m^{-3}	kg m^{-3}
0	1.292	1.289
5	1.269	1.265
10	1.246	1.240
15	1.225	1.217
20	1.204	1.194
25	1.183	1.169
30	1.164	1.145
40	1.128	1.096

Does a baseball fly Less far on a humid day?

Density of air, moist and dry. Baseball players claim the air is heavy on humid days so the ball may not travel as far when hit. Is this true? Is the air more or less dense on a humid day? We see the air is less dense on a humid day, so it should exert less drag on the ball and it should fly a bit farther.

Water Potential of atmospheric humidity is function of its mole fraction

$$\psi_p = \frac{R \cdot T}{V_w} \ln(\frac{e_a}{e_s(T)})$$



R: Universal gas constant, J K^{-1} mol^{-1}
T: absolute temperature
e_a: vapor pressure
P: pressure
V_w: molal volume of water, 18.05 10^{-6} m^3 $mole^{-1}$

What is the water potential of boiling water?

Biometeorology, ESPM 129

What is the water potential of boiling water? Technically it should be zero as the definition of boiling is when the saturation vapor pressure equals atmospheric pressure. The natural log of 1 is zero.

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
R is universal gas constant

m_c is the molecular mass (g $mole^{-1}$) of the compound.

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

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

n_c is the number of moles
V is volume

m_c is the molecular mass (g mole^{-1}) of the compound.

Mass fraction (mass per unit mass of air)

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

m_a is the molecular weight of dry air (g mol^{-1})
m_c is molecular weight of trace gas
ρ_a is the mass density of dry air (g m^{-3})
ρ_c is the mass density of trace gas air (g m^{-3})

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

Moist air

$$C_c = \frac{n_c}{n} = \frac{m_a}{m_c}\frac{\rho_c}{\rho} = \frac{p_c}{p}$$

Dry air

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

Biometeorology, ESPM 129

Mixing Ratio of Water Vapor, Saturated Atmosphere

T	dry	Saturation vapor pressure		Mixing Ratio
°C	Kg m^{-3}	g m^{-3}	mmol m^{-3}	ppt
0	1.292	4.85	269	6.02
5	1.269	6.8	377	8.60
10	1.246	9.4	522	12.1
15	1.225	12.07	670	15.8
20	1.204	17.31	961	23.1
25	1.183	23.06	1281	31.3
30	1.164	30.4	1688	41.9
40	1.128	51.2	2844	72.9

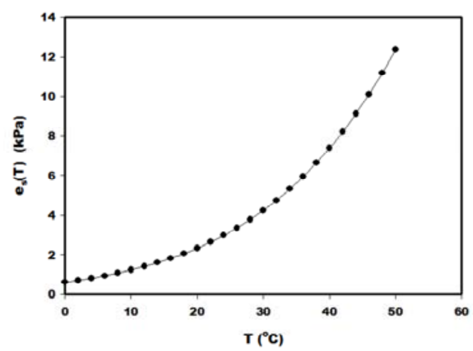
Saturation Vapor Pressure

- 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.

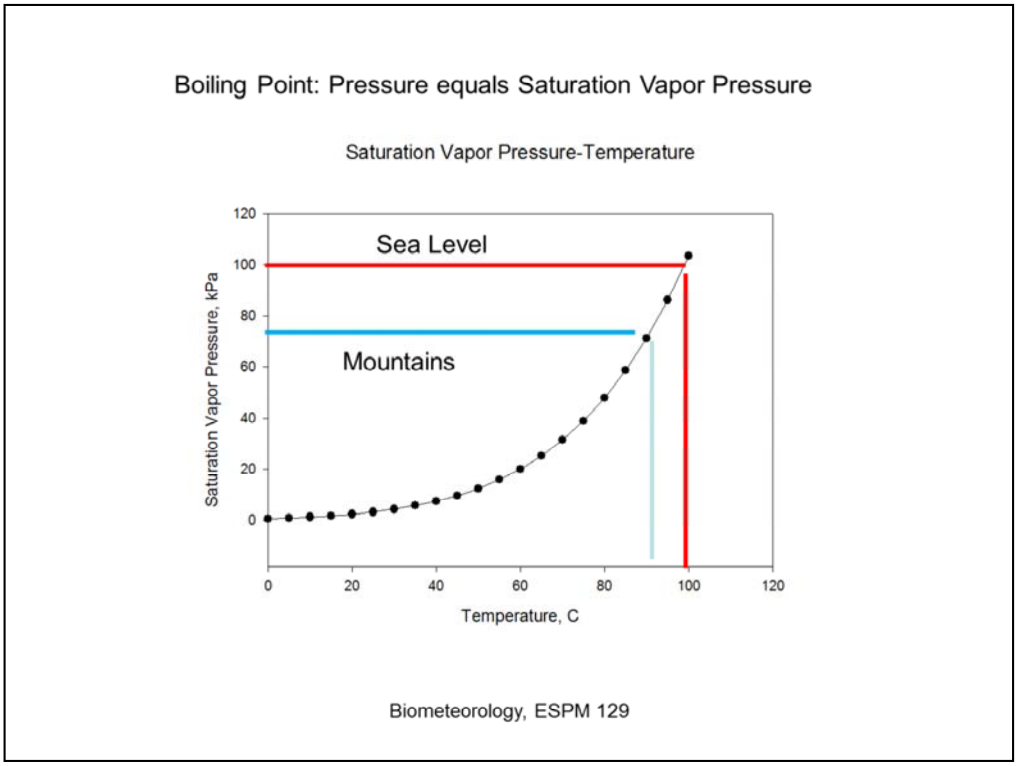
Saturation Vapor Pressure-Temperature Function

$$e_s(T_c) = a\exp\left(\frac{bT_c}{c+T_c}\right) \quad \text{kPa}$$

Over Water	Over Ice
a=0.611	a=0.611
b= 17.502	b= 21.87
c=240.97	c=265.5



This is an important equation which is used a lot in biometeorology. You don't need to memorize it, but do feel comfortable to use it and recognize that saturation vapor pressure is an exponential function of temperature



Boiling point in the mountains occurs at lower temperatures than at sea level. Hence it is really difficult to cook good pasta in the high moutains.

Slope of Saturation Vapor Pressure-Temperature Curve

$$\frac{de_s(T)}{dT} = s = \frac{0.611 \cdot 17.502 \cdot 240.97 \cdot \exp\left(\frac{17.502 \cdot T}{240.97 + T}\right)}{(240.97 + T)^2}$$

e_s, saturation vapor pressure, kPa
e_a, vapor pressure
h_r, relative humidity
s, slope of e_s vs T relation
T, temperature, C
T_a, air temperature
T_s, surface temperature

Biometeorology ESPM 129

We will use the slope of the saturation vapor pressure curve to estimate evaporation rates.

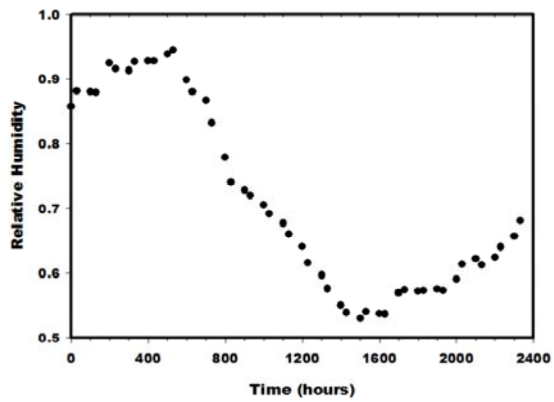
Relative Humidity, h_r,

the ratio between the actual (e_a) and saturation vapor pressures ($e_s(T)$).

It ranges between zero and 1.0, with one indicating saturation.

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

$e_a = p_{H2O}$

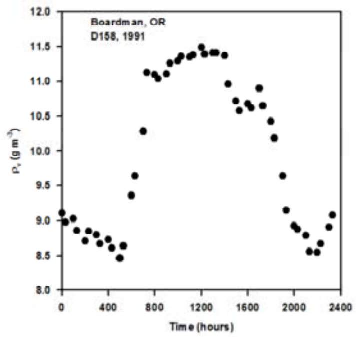


Biometeorology, ESPM 129

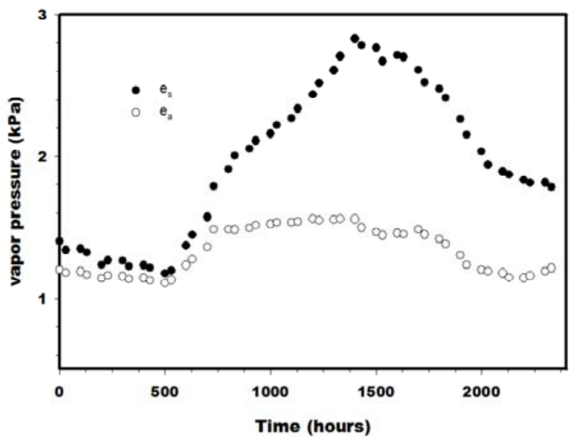
Absolute humidity or vapor density (g m^{-3}):

$$\rho_v = \frac{e_a m_v}{R T_k} \qquad \rho_v(g \cdot m^{-3}) = \frac{2.165 \cdot e_a(kPa)}{T_k}$$

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

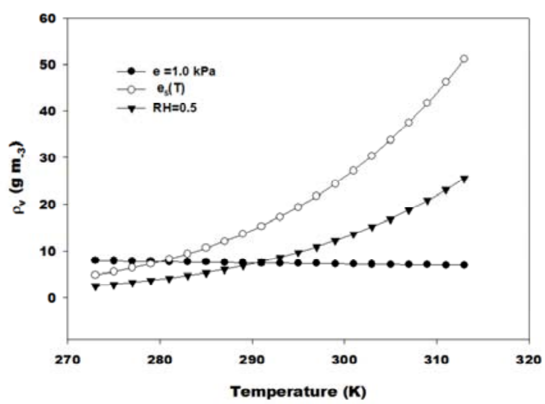


Biometeorology, ESPM 129



vapor pressure (kPa)
Time (hours)
e_s
e_a
0
500
1000
1500
2000
1
2
3

Humidity vs Temperature



Biometeorology, ESPM 129

Virtual Temperature.
is the temperature **dry air would have**
if it had the same density as moist air at the same pressure

it is related to the **speed of sound**

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

and

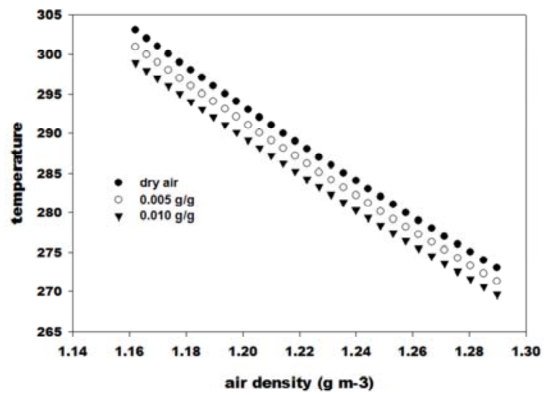
buoyancy of the air.

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

$$\frac{\rho'}{\overline{\overline{\rho}}} = \frac{T_v'}{\overline{\overline{T_v}}}$$

Acceleration, a

Air Temperature and Virtual Temperature



Biometeorology, ESPM 129

Virtual Temperature is the Temperature Dry air would have if its Pressure and specific volume were equal to those of a sample of moist air

Derivation: Virtual Temperature

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

$$T_v = \frac{T}{1 - \frac{e}{P}\left(1 - \frac{m_v}{m_a}\right)}$$

Biometeorology, ESPM 129

Chemical Potential of Water

Chemical potential quantifies
the driving force for movement of water between two locations

The chemical potential of water is related to the amount of change in the Gibbs free energy of the system, subjected by pressure, temperature and minor constituents
, e,g., salts, .
It relates to the free energy needed for a transition from State A to B

It is a function of its chemical concentration, pressure, electrical potential and gravity

The chemical potential has units of energy (J mol^{-1}).

Water Potential

The **potential energy** of water is related to the difference between its chemical potential (μ_w) and a reference state (μ_{wo}):

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

By convention, Water potential is normalized by V_w, the partial molal volume of water ($18.05\ 10^{-6}\ m^3\ mol^{-1}$), giving it units of **Pressure**.

Chemical Potential is a function of:

Chemical activity: RT ln(a); a = vC
Pressure: (VP)
Electrical Potential: (zPE)
Gravity: (mgh)

$$\mu = \mu_0 + RT\ln(a) + VP + zFE + mgh$$

The **total water potential** of a system consists of the sum of water potentials associated with

Turgor (pressure), **osmotic**, **matrix** and **gravitational** forces

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

Units, Pressure: Pa