2. Chemical Hydrology

A. A cylindrical soil core ($L = 20\ cm,\ r = 3\ cm$) was collected from a field site in Madison County, Iowa, The weight of the empty metal cylinder is: $m_1 = 225\ g$. The metal cylinder containing field-moist soil is weighed ($m_2 = 1217.8\ g$) then dried in a 100°C oven until it ceases to lose weight. The weight of the cylinder containing oven-dried soil is: $m_3 = 977.1\ g$.

Calculate: 1) the mass water content w_{fm} $[Mg \cdot Mg^{-1}]$ of the field moist soil and 2) the *moist* soil bulk density ρ_t $[Mg \cdot m^{-3}]$.

Solution

Part 1. Compute the mass water content of field moist soil w_{fm}.

The mass water content of the field moist soil w_{fm} is the water loss on drying m_w divided by the dry soil mass m_s. The dry mass must account for the mass of the container.

$$m_w = m_2 - m_3 = 1217.8\ g - 977.1\ g = 240.7\ g \tag{2.1}$$

$$m_s = m_3 - m_1 = 977.1\ g - 225.0\ g = 752.1\ g \tag{2.2}$$

$$w_{fm} = \frac{m_w}{m_s} = \frac{240.7\ g}{752.1\ g} = 0.320 \tag{2.3}$$

Part 2. Compute the moist soil bulk density ρ_t.

The field-moist bulk density ρ_t is field-moist soil mass m_{fm} divided by the container volume V_{fm}.

$$V_{fm} = \pi \cdot r^2 \cdot L = \pi \cdot 9\ cm^2 \cdot 20\ = 565.5\ cm^3 \tag{2.4}$$

$$\rho_t = \frac{m_2 - m_1}{V_{fm}} \tag{2.5}$$

$$\rho_t = \frac{1217.8\ g - 225.0\ g}{565.5\ cm^3} = 1.76\ g \cdot cm^3 \tag{2.6}$$

The units $[g \cdot cm^3]$ are not SI Units however field-moist bulk density ρ_t in SI units is numerically equal to the value quoted above.

$$\rho_t = 1.76\ g \cdot cm^3 = 1.76\ Mg \cdot m^3 \tag{2.7}$$

B. A cylindrical soil core ($L = 20\ cm,\ r = 3\ cm$) was collected from a field site in Madison County, Iowa, The weight of the empty metal cylinder is: $m_1 = 225\ g$. The metal cylinder containing field-moist soil is weighed ($m_2 = 1217.8\ g$) then dried in a 100°C oven until it ceases to lose weight. The weight of the cylinder containing oven-dried soil is: $m_3 = 977.1\ g$.

Calculate: 1) the *moist* porosity ϕ and 2) the *volumetric* water content θ_{fm} $[m^3 \cdot m^{-3}]$.

Solution

Part 1. Compute the porosity of field moist soil ϕ_{fm}.

Drying alters the volume of many soils with relatively high clay contents. This volume change is quantified as the *coefficient of linear extensibility C.O.L.E.* by the soil science community and and the *shrinkage limit* by the geotechnical community.

The field-moist soil volume is V_{fm} simply the container volume.

$$V_{fm} = \pi \cdot r^2 \cdot L = \pi \cdot 9\ cm^2 \cdot 20\ = 565.5\ cm^3 \tag{2.8}$$

The solids volume V_s, regardless of water content, is dry solids mass m_s divided by the solids density ρ_s. The soil science community uses the density of the mineral quartz $SiO_2(s)$ as the default density for all soil minerals: $\rho_s \equiv \rho_{SiO_2(s)} = 2.65\ Mg \cdot m^{-3}$.

$$m_s = m_3 - m_1 = 977.1\ g - 225.0\ g = 752.1\ g \tag{2.9}$$

$$V_s = \frac{m_s}{\rho_s} = \frac{752.1\ g}{2.65\ g \cdot cm^{-3}} = 283.8\ cm^3 \tag{2.10}$$

The field-moist porosity ϕ_{fm} is simply void volume under field-moist conditions divided by the field-moist volume V_{fm}.

$$\phi_{fm} = \frac{V_{fm} - V_s}{V_{fm}} = \frac{565.5\ cm^3 - 283.8\ cm^3}{565.5\ cm^3} = 0.498\ cm^3 \cdot cm^{-3} \tag{2.11}$$

Part 2. Compute the field-moist *volumetric* water content θ_{fm} $[m^3 \cdot m^{-3}]$.

The *volumetric* water content θ_{fm} $[m^3 \cdot m^{-3}]$ is computed in much the same was as the solids volume V_s. The field-moist water volume V_w is the water mass m_w divided by water density ρ_s.

$$m_w = m_2 - m_3 = 1217.8\ g - 977.1\ g = 240.7\ g \tag{2.12}$$

$$V_w = \frac{m_w}{\rho_w} = \frac{240.7\ g}{0.997\ cm^3} = 241.4\ cm^3 \tag{2.13}$$

$$\theta_{fm} = \frac{V_w}{V_{fm}} = \frac{241.4\ cm^3}{565.5\ cm^3} = 0.427\ cm^3 \tag{2.14}$$

NOTE: Chapter 2 (*Chemical Hydrology*) expression (13) offers an alternative method for computing field-moist volumetric water content θ_{fm} using the mass water content w_{fm} and *dry bulk density* ρ_b. In the present case the dry bulk density ρ_b is not quoted and, therefore, expression (13) would not be an appropriate method.

C. Table 2.1 lists the physical and water retention data for the Macksburg soil series from Madison County Iowa. The Macksburg soil is located on nearly level (0-2% slopes) upland sites, has moderately high permeability and is considered well drained.

Table 2.1: Moist bulk density ρ_t and mass water contents w of the Macksburg soil from Madison County, Iowa. Mass water content at $p_{tension} = -33\ kPa$ is w_{33} and mass water content at $p_{tension} = -1500\ kPa$ is w_{1500}.

Horizon	ρ_t $Mg \cdot m^{-3}$	w_{33} $Mg \cdot Mg^{-1}$	w_{1500} $Mg \cdot Mg^{-1}$
0-15 cm	1.55	0.273	0.153
15-30 cm	1.40	0.278	0.160
30-61 cm	1.50	0.297	0.168
61-91 cm	1.52	0.292	0.180
91-107 cm	1.53	0.297	0.169

Determine the volumetric plant-available water-holding capacity θ_{AWC} of the Macksburg soil profile, reporting the water-holding capacity as centimeters of water for the 107 cm soil depth.

Solution

Table 2.1 quotes the *moist* bulk density ρ_t of each soil horizon, allowing the use of expression (13) to compute the volumetric plant-available water-holding capacity θ_{AWC} of each horizon and the entire profile.

$$\rho_b = \frac{\rho_t}{1 + w_{33}} \tag{2.15}$$

$$\theta_{AWC} = (w_{33} - w_{1500}) \cdot \left(\frac{\rho_b}{\rho_w} \right) \tag{2.16}$$

$$d_{AWC} = \theta_{AWC} \cdot d_t \tag{2.17}$$

The method is illustrated for the Ap horizon (0-15 cm depth).

Horizon A1

$$\rho_b^{\text{Ap}} = \frac{1.55}{1+0.273} = 1.22\ Mg \cdot m^{-3} \tag{2.18}$$

Horizon A1

$$\theta_{AWC}^{\text{Ap}} \approx (0.273 - 0.153) \cdot \left(\frac{1.22}{1.00}\right) = 0.146\ m^3 \cdot m^{-3} \tag{2.19}$$

$$d_{AWC}^{\text{Ap}} = \left(0.146\ cm_{water} \cdot cm_{soil}^{-1}\right) \cdot 15\ cm_{soil} = 2.19\ cm_{water} \tag{2.20}$$

Table 2.2: Moist bulk density ρ_t, mass water contents w and volumetric *plant-available water-holding capacity* of the Macksburg soil from Madison County, Iowa. Mass water content at $p_{tension} = -33\ kPa$ is w_{10} and mass water content at $p_{tension} = -1500\ kPa$ is w_{1500}.

d_t cm	ρ_t $Mg \cdot m^{-3}$	w_{AWC} $Mg \cdot Mg^{-1}$	θ_{AWC} $cm_{water} \cdot cm_{soil}^{-1}$	d_{AWC} cm_{water}
15	1.22	0.120	0.147	2.20
15	1.10	0.118	0.130	1.94
31	1.16	0.129	0.150	4.64
30	1.18	0.112	0.132	3.96
16	1.18	0.128	0.151	2.42

Table 2.2 lists the volumetric plant-available water-holding capacity θ_{AWC} of each horizon in column 5. The plant-available water-holding capacity as an equivalent water depth of 15.17 cm for the entire horizon is the sum of horizon equivalent-depths d_t appearing in column 6.

Macksburg Soil Profile

$$d_{AWC}^{\text{profile}} = (2.19 + 1.94 + 4.64 + 3.96 + 2.42)\ \ cm_{water} = 15.17\ cm_{water} \tag{2.21}$$

D. The Robbs soil from Johnson County, Illinois has a moist bulk density of $\rho_t = 1.34\ Mg \cdot m^{-3}$ and a field-capacity volumetric water content of $\theta_{fc} =$

0.38 $cm{\cdot}cm^{-1}$. The solids-water partition coefficient for the herbicide Cyanazine (CAS Registry Number 21725-46-2) in the Robbs soil is: $K^{\ominus}_{\mathrm{s/w}} = 2.2\ m^3 \cdot Mg^{-1}$.

Calculate the Cyanazine retardation coefficient R_{f} for the Robbs soil at field capacity.

Solution

Chapter 2 (*Chemical Hydrology*) gives the retardation coefficient as expression (33).

$$R_{\mathrm{f}} = \left(1 + \left(\frac{K^{\ominus}_{\mathrm{s/w}} \cdot \rho_t}{\theta_{fc}}\right)\right) \tag{2.22}$$

$$R_{\mathrm{f}} = \left(1 + \left(\frac{2.2 \cdot 1.30}{0.38}\right)\right) = 8.74 \tag{2.23}$$

E. The Macksburg soil (Madison County, Iowa) has a retardation coefficient of $R_{\mathrm{f}} = 42.2$ for the herbicide Atrazine (CAS Registry Number 1912-24-9). In early spring the Macksburg soil is at field capacity and the depth to water table is 45 cm.

Estimate how deep Atrazine applied at the surface of Macksburg soil will migrate after a 7.6 cm rainfall under prevailing conditions.

Solution

When the soil content is at field capacity it has no water storage capacity. The wetting depth, therefore, for the 7.6 cm rainfall is the depth to water table: $L_w = 45\ cm$.

$$R_{\mathrm{f}} \equiv \frac{L_w}{L_A} \tag{2.24}$$

$$L_A = \frac{L_w}{R_{\mathrm{f}}} = \frac{45\ cm}{42.2} = 1.07\ cm \tag{2.25}$$

Percolating water will transport Atrazine to a depth of 1.07 cm in the Mackesburg as the wetting front travels to the water table at a depth of 45 cm.

F. The Antigo soil (Langlade County, Wisconsin) has a retardation coefficient of $R_{\mathrm{f}} = 3.90$ for the organophosphate insecticide Phosmet (CAS Registry Number 732-11-6). The Antigo soil has a field capacity water content of $\theta_{fc} = 0.37\ cm \cdot cm^{-1}$.

Estimate how deep Phosmet applied at the surface of Antigo soil will migrate after a 3.27 cm rainfall. The soil water content as rain begins to fall is: $\theta_{fm} = 0.20\ cm \cdot cm^{-1}$.

Solution

The water storage capacity ΔS of the Antigo soil is the difference between the water content at field capacity θ_{fc} and the water content θ_{fm} on the date rain begins to fall.

$$\Delta S = \theta_{fc} - \theta_{fm} \tag{2.26}$$

$$\Delta S = (0.37 - 0.20)\ \ cm \cdot cm^{-1} = 0.17\ cm_{water} \cdot cm_{soil}^{-1} \tag{2.27}$$

The wetting depth L_w following a 3.27 cm rainfall is found by dividing the rainfall depth by soil water storage capacity.

$$L_A = \frac{d_w}{\Delta S} = \frac{3.27\ cm_{water}}{0.17\ cm_{water} \cdot cm_{soil}^{-1}} = 19.2\ cm_{soil} \tag{2.28}$$

The Phosmet leaching depth $L_A = 4.92\ cm$ following a 3.27 cm rainfall is found using the retardation coefficient expression.

$$R_{\mathrm{f}} \equiv \frac{L_w}{L_A} \tag{2.29}$$

$$L_A = \frac{L_w}{R_{\mathrm{f}}} = \frac{19.2\ cm_{soil}}{3.90} = 4.92\ cm_{soil} \tag{2.30}$$

G. The volumetric moisture content of a fine-sand soil is $\theta = 0.12\ m^3 \cdot m^{-3}$.

Use the empirical Clapp-Hornberger water retention function in Appendix D to estimate the tension head $h_{tension}$ at this water content.

Solution

Clapp and Hornberger (1978) published parameters for eleven (11) different soil texture classes required by their empirical water-retention function.

Table 2.3: Clapp-Hornberger water-retention parameters for the sand texture class.

ϕ	h_s cm	b
0.395	12.10	4.05

One of these eleven parameters is porosity ϕ. The independent variable for the empirical water-retention function is the *degree of saturation* s.

$$s_{fm} = \frac{\theta_{fm}}{\phi} = \frac{0.12}{0.395} = 0.304 \tag{2.31}$$

The tension head is, by definition, less than zero: $h_{tension} < 0$. The Clapp-Hornberger water-retention function yields the absolute value of the tension head: $|h_{tension}|$.

$$|h_{tension}| = h_s \cdot \left(\frac{\theta_{fm}}{\phi}\right)^{-b} = h_s \cdot s^{-b} \tag{2.32}$$

$$|h_{tension}| = 12.10\ cm \cdot (0.304)^{-4.05} = 1510\ cm \tag{2.33}$$

The tension head at field capacity is: $h_{tension} \approx -100\ cm$. The tension head at the wilting point is: $h_{tension} \approx -15300\ cm$.

H. Use the empirical Clapp-Hornberger unsaturated hydraulic conductivity function in Appendix D to estimate the hydraulic conductvity k_D of a loam-texture soil at field capacity.

Solution

Clapp and Hornberger (1978) published parameters for eleven (11) different soil texture classes required by their empirical unsaturated hydraulic-conductivity function.

Table 2.4: Clapp-Hornberger hydraulic conductivity parameters for the loam texture class.

ϕ	h_s cm	K $mm \cdot hour^{-1}$	b
0.451	12.10	25.02	5.39

One of these eleven parameters is porosity ϕ. The independent variable for the empirical water-retention function is the *degree of saturation s*.

$$\theta_{fc} = \phi \cdot \left(\frac{h_s}{|h_{tension}|} \right)^{1/b} \tag{2.34}$$

$$\theta_{fc} = 0.451 \cdot \left(\frac{5.39}{|-100\ cm|} \right)^{1/5.39} = 0.392 \tag{2.35}$$

$$s_{fc} = \frac{0.392}{0.451} = 0.869 \tag{2.36}$$

The *degree of saturation s* is the independent variable for the empirical unsaturated hydraulic-conductivity function.

$$K_D = K_s \cdot s^{2 \cdot b + 3} \tag{2.37}$$

$$K_D = \left(25.02\ mm \cdot hour^{-1}\right) \cdot (0.869)^{2 \cdot (5.39) + 3} = 3.61\ mm \cdot hour^{-1} \tag{2.38}$$

I. Use the Thornthwaite potential evapotranspiration model to estimate the mean evapotranspiration water loss during May 2016 in Dane County, Wisconsin. Identify the weather station you use to make your estimate.

Solution

The Thronthwaite model (below) relies on a two site-specific parameters and the immediate mean monthly temperature to estimate potential evaportranspiration on a monthly time scale. Mean monthly day length $\overline{L}_m$ is determined by site longitude.

$$PET\ [cm \cdot month^{-1}] = 1.6 \cdot \left(\frac{\overline{L}_m}{12}\right) \cdot \left(\frac{N_m}{30}\right) \cdot \left(\frac{10 \cdot \overline{T}_m}{I}\right)^{a(I)} \tag{2.39}$$

The heat index I is a function of long-term mean monthly temperatures for the entire year. A reliable estimate of site heat index I requires 10, 20 or more years of data to compute long-term mean monthly temperatures.

The National Climate Data Center (U.S. National Oceanic and Atmospheric Administration) *Climate Data Online* is the source of 20 years of monthly mean temperatures (Table 2.5) recorded at the Dane County Regional Airport MSN (NCDC Station USW00014837), Madison, WI.

$$I = \sum_{m=1}^{12} \left(\frac{\overline{T}_m}{5}\right)^{1.514} \tag{2.40}$$

Table 2.5: Monthly mean temperatures for Dane County Regional Airport MSN, Madison, Wisconsin (NCDC Station USW00014837). The period was from January 1996 through December 2015. Source: NCDC Climate Data Online

Month	$\overline{T}_m$	Month	$\overline{T}_m$
	°C		°C
JAN	-6.78	JUL	21.41
FEB	-5.02	AUG	20.33
MAR	0.88	SEP	16.22
APR	8.04	OCT	9.63
MAY	13.86	NOV	2.99
JUN	19.27	DEC	-3.75

The heat index for Dane County Regional Airport MSN, Madison, Wisconsin (NCDC Station USW00014837), computed using data listed in Table 2.5 and expression (2.40), is: $I = 40.99$. Exponent $a(I)$, a function of the site heat index I, is computed using the coefficients listed in Table 2.6 and the following expression.

Table 2.6: Coefficients for exponent $a(I)$ appearing in expressions (2.37) and (2.38).

Coefficient	Value
a_0	0.49239
a_1	$1.7921 \cdot 10^{-2}$
a_2	$7.711 \cdot 10^{-5}$
a_3	$6.751 \cdot 10^{-7}$

$$a(I) = a_0 \cdot I^0 + a_1 \cdot I^1 + a_2 \cdot I^2 + a_3 \cdot I^3 \tag{2.41}$$

The mean monthly temperature for May 2016 in Dane County, Wisconsin was: $\overline{T}_m = 15.0\ °C$. The mean day length for May at Dane County Regional Airport is $\overline{L}_m = 14.12\ hours$. The mean monthly potential evapotranspiration is $PET = 8.6\ cm \cdot month^{-1}$ or $PET = 0.28\ cm \cdot day^{-1}$.

$$PET = 1.6 \cdot \left(\frac{14.12}{12}\right) \cdot \left(\frac{31}{30}\right) \cdot \left(\frac{10 \cdot 15.0}{40.99}\right)^{1.14} = 8.6\ \ cm \cdot month^{-1} \tag{2.42}$$

J. The estimated evapotranspiration water loss during June 2008 in a Dane County, Wisconsin watershed averaged 4.9 mm of water per day. The average soil depth in the watershed is 100 cm and has a total water storage capacity of: $\theta = 0.400\ cm \cdot cm^{-1}$. At the beginning of June 2008 the soil moisture content in the watershed averaged $\theta_{initial} = 0.370\ cm \cdot cm^{-1}$.

Predict stream discharge from this watershed at the end of June 2008 during which 167.6 mm of precipitation fell.

Solution

Table 2.7 lists the soil water balance parameters for Gordon Creek catchment during June 2008.

Table 2.7: Water balance parameters for the Gordon Creek catchment (Dane County, Wisconsin) during June 2008.

Parameter	Symbol	Value	Units
Precipitation	P	167.6	mm
Daily Evapotranspiration	ET	4.9	$mm \cdot day^{-1}$
Field-Capacity Water Content	θ_{fc}	0.400	$mm \cdot mm^{-1}$
Initial Water Content	θ_i	0.370	$mm \cdot mm^{-1}$
Soil Profile Depth	d_{soil}	100	cm

The soil profile water storage capacity at the end of May 2008 is $\Delta S_i = 30.48\ mm$.

$$\Delta S_i = (\theta_{fc} - \theta_i) \cdot d_{soil} \tag{2.43}$$

$$\Delta S_i = \left(0.400 - 0.370\ mm \cdot mm^{-1}\right) \cdot 1000\ mm = 30.48\ mm \tag{2.44}$$

The water *surplus* (or *deficit*) at the end of June 2008 is the difference between precipitation minus the evapotranspiration water loss for the entire month.

$$ET = \left(4.9\ mm \cdot day^{-1}\right) \cdot 30\ day = 146.0\ mm \tag{2.45}$$

$$P - ET = 167.6\ mm - 146.0\ mm = 21.6\ mm \tag{2.46}$$

The June 2008 water surplus is less than the soil profile water storage capacity at the beginning of month: $(P - ET) < \Delta S_i$. Stream discharge D that can be attributed to precipitation minus evapotranspiration water loss is zero.
