EFFECT OF DESORPTION AND SORPTION PROCESSES OCCURRING IN A DRY SOIL LAYER ON THE VARIATION OF WATER EVAPORATION

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The effect of desorption and sorption processes accompanying temperature changes in a dry layer of natural soil on the transport of vapor in the soil is discussed and the temporal variation of the evaporation of water from the soil is explained.

Up to now a theory of the evaporation of water from soil has not been developed [1-3]. The difficulty of this problem, as Anderson [4] sees it, is associated with the complexity of environmental processes, the absence of data, and the inadequacy of our knowledge of the physics of evaporation processes. A most important problem which should be explained by the theory is the temporal (diurnal) variation of the evaporation of water from soil with a dried-out layer of the surface. In the present paper it is shown to be possible to explain the temporal variation of the evaporation of water from the soil by solving the diffusion equation, taking into account desorption and sorption processes which occur when the temperature changes in a layer of dry soil.

The evaporation of water from soil with a dry surface layer is evidently due to the transfer of water vapor in the soil. A modern theory of heat and mass transfer has been developed by A. V. Lykov and his school [5-8]. Heat transfer uncomplicated by mass transfer is explained by the heat-transfer potential (temperature). A. V. Lykov [6] suggested the introduction of the concept of mass-transfer potential which permits describing mass transfer in the same manner.

The concept of thermodynamic force, defined as the gradient of the pertinent potential, is introduced in the thermodynamics of nonequilibrium states. The transfer of a substance is explained by the action of several thermodynamic forces and as a consequence of this different types of transfers, which are considered separately in classical physics, prove to be interrelated processes. In particular, the transfers of heat and mass are processes affecting each other. The effect of heat transfer on mass transfer, manifested as thermal diffusion, was first noted and proved experimentally in [9]. The essence of the phenomenon of thermal diffusion in a capillary-porous medium consists in that the temperature affects the distribution of moisture in a material and thereby the transfer of matter. Nonisothermal mass transfer in a capillary-porous medium, in particular, moisture into soil, represents a superposition of concentration diffusion and thermal diffusion.

The differential equations of heat and mass transfer, reduced on the basis of the general theory of similarity to a dimensionless form, are considered jointly in modern transfer theory. A. V. Lykov and his pupils solved a comparatively wide range of heat- and mass-transfer problems for different boundary conditions having practical value. In particular, a system of differential equations of heat and mass transfer in soil for boundary conditions given on the soil surface and at infinity was solved in [8]. In the general case the solution of the system of differential equations of heat and mass transfer, as noted in [8], presents major mathematical difficulties. In those cases when the problem is solved analytically to the end, the results obtained are generally rather complex expressions. It is possible to simplify the problem considerably [8] if the system of equations of heat and mass transfer is reduced to two unrelated equations by means of a new variable introduced as a linear combination of transfer potentials. Heat and mass transfers are considered separately in the first approximation, if in the system of linear Onsager equations corresponding

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to the problem the terms with kinetic coefficients of cross indexes characterizing the interrelationship of the flows of energy and matter are small. Obviously, in some cases the possibility of describing mass transfer independently of heat transfer can be achieved on the basis of the characteristics of the problem under consideration. In particular, in a dry soil layer, moisture can move only as vapor [10, 11] and the transfer of matter should be described by the diffusion equation. The mechanism of the formation and movement of vapor in a layer of dry soil allows the differential equation of diffusion to be written with consideration of the effect of temperature on vapor transfer, as is done below.

Soil is considered dry [2, 12] if its moisture content is less than the maximum hygroscopicity (MH). The thickness on the dry layer formed on the surface of natural soil should be determined as the distance h from the soil surface to the level at which the soil moisture content is equal to MH. During the diurnal change of temperature in the layer of dry soil there occur desorption and sorption processes, which act as internal vapor sources (positive or negative). The formation and movement of water vapor in the layer of dry soil should be described by the equation

$$\frac{\partial q}{\partial \tau}=D\frac{\partial^2 q}{\partial z^2}+w(z,\ \tau),\quad 0\leqslant\tau\leqslant T,\ 0\leqslant z\leqslant h, \tag{1}$$

where $w(z, \tau)$ is the specific power of the internal sources. If we take the vapor density (volume concentration) as the state parameter of the vapors contained in the soil pores q, in Eq. (1) D will be the effective diffusion coefficient determined by H. Penman's formula [13].

The formation and absorption of vapors occurring in a dry soil layer as a consequence of desorption and sorption processes were studied experimentally under field conditions. The results of these experiments are discussed in [12], where it is shown that the specific power of the internal sources can be described by an empirical formula in terms of the rapidity of the change of soil temperature or in terms of the change of the distribution of sorbed moisture due to desorption and sorption processes. It follows from the experiments that the specific power of the internal sources, represented by the rapidity of the change of temperature, is practically independent of the coordinate. Actually, on the graph (shown in [12]) the curves of the distribution of sorbed moisture over the soil profile at different times of the same day are arranged more or less parallel to one another. Consequently, drying and moistening of the profile of the hygroscopic region occurring, respectively, in the heating and cooling stage of the soil take place more or less similarly at all levels of the dry soil layer. Hence it follows that, for the changes of soil temperature observed under natural conditions, we can consider the specific power of the internal sources to be practically independent of the coordinate. In [12], to determine the specific power of internal sources, an empirical formula of the following form is suggested:

$$w(\tau)=\frac{\chi_0}{1+\varkappa h}\cdot\frac{\partial t(\tau)}{\partial\tau}, \tag{2}$$

where $t(\tau)$ is a function known from observational data, representing the approximation of the temporal (diurnal) change of temperature on the soil surface (or at any other given level). The coordinate-independence of the specific power of the internal sources is easily explained in that the temperature wave decays on propagating into the soil, but in this case the mass of vapors formed upon a 1° change of temperature increases owing to an increase of soil moisture.

The formation of a dry layer on the surface of natural soil obviously begins at the time when the soil moisture content decreases to MH, and therefore in the problem under consideration the initial conditions can be given in the form

$$q(z,\ 0)=q_m. \tag{3}$$

The law of convective mass transfer on the surface of soil is very complex [2, 8]. The boundary conditions for $z = 0$ can be formulated in the first approximation as Newton's law

$$D\left.\frac{\partial q}{\partial z}\right|_{z=0}=\alpha(q-q_a)_{z=0}. \tag{4}$$

From the solution of Eq. (1) it is easy to derive, as is done below, the formula of the temporal variation of evaporation, which when $h = 0$ should describe evaporation from the surface of moist soil. It turns out that, for the boundary condition given in the form of (4), a formula of evaporation is obtained from the solution of the equation which at the limit, when $h \to 0$, changes to the empirical formula proposed by many investigators [2, 3], evaporation from the surface of moist soil is similar to that from an open water surface. Thus there is a definite objective premise necessitating the choice of the boundary condition in the form of (4) in the problem being considered.

As is known [2, 14], saturated vapors are present in the pores of moist soil. Considering the vapor density field at the level of the lower edge of the dry soil layer ($z = h$) to be continuous, we can give the second boundary condition in the form

$$q_{z=h} = q_s (h, \tau). \tag{5}$$

The law of propagation of the temperature wave in soil is known [8, 15], and therefore from the temperature of the soil surface we find the temperature at level $z = h$ needed for determining the density of the saturating vapors $q_s(h, \tau)$ by Magnus' formula [3]. When the boundary condition is given in the form of Eq. (5) and the specific power of the internal sources is represented in the form of Eq. (2), the thickness of the dry layer h – one of the most important parameters on which the magnitude of water evaporation from the soil under natural conditions unconditionally depends – proves to be introduced into the problem. As a rule the thickness of the dry layer formed on the soil surface is not very large, and for the boundary conditions given in the form of Eqs. (4) and (5) it will be valid to use the method of zonal calculation on the assumption that the entire hygroscopic region of soil represents one zone.

It is necessary to note that thermal diffusion – the effect of temperature on vapor transfer in the dry soil layer – is taken into account in the problem under consideration. Actually, change of temperature in the dry soil layer is accompanied by desorption and sorption processes which tend to equalize the gradient of the vapor density and establish a mode of steady-state diffusion [12]. The effective surface of the soil particles is large, and the formation and absorption of vapors in the dry soil layer in the case of the temperature changes observed under natural conditions occurs in the presence of insignificant deficits. As a result, at any instant the vapor density is distributed in practice according to the linear law uniquely defined by the conditions given on the boundaries of the dried layer of soil. A change of boundary condition (5) in relation to the variation of temperature is reflected appropriately in the distribution of vapors over the profile of the dry soil layer. Thus; in the problem under consideration, the effect of temperature on the vapor distribution and, consequently, on vapor transfer in the dry soil layer, where the possibility of movement of the moisture in a liquid form is ruled out, is taken into account by the boundary condition given in the form of Eq. (5). The effect of a change of temperature on mass transfer is taken into account directly by the second term on the right side of Eq. (1).

The thickness of the dry layer during a 24 h period changes [12]. If we neglect the relatively small diurnal fluctuation of the thickness of the dry soil layer, Eq. (1) is easily solved by the operational method. In solving the problem under consideration the variation of temperature on the soil surface and the function of the saturating vapor density $q_s(h, \tau)$ were presented in the form of a Fourier series. The solution of Eq. (1) for boundary conditions (3)-(5) and under the assumption that the thickness of the dry layer does not change has the form

$$\begin{aligned}
q(z, \tau) = {} & \frac{q_0 (h - z) + B_0 \left(z + \frac{1}{\alpha'} \right)}{h + \frac{1}{\alpha'}} + \frac{\chi_0}{1 + \varkappa h} \sum_{n=1}^{\infty} A_n \sin n\omega (\tau - \tau_n) \\
& - \frac{\chi_0}{1 + \varkappa h} \sum_{n=1}^{\infty} A_n \{ \{ [\mathrm{sh}\, \beta_n (h - z) \cos \beta_n (h - z) + X (\beta_n z)] X (\beta_n h) \\
& + [\mathrm{ch}\, \beta_n (h - z) \sin \beta_n (h - z) + Y (\beta_n z)] Y (\beta_n h) \} / [X^2 (\beta_n h) + Y^2 (\beta_n h)] \} \\
& \times \sin n\omega (\tau - \tau_n) + \frac{\chi_0}{1 + \varkappa h} \sum_{n=1}^{\infty} A_n \{ \{ [\mathrm{sh}\, \beta_n (h - z) \cos \beta_n (h - z) \\
& + X (\beta_n z)] Y (\beta_n h) - [\mathrm{ch}\, \beta_n (h - z) \sin \beta_n (h - z) + Y (\beta_n z)] X (\beta_n h) \} / [X^2 (\beta_n h) \\
& + Y^2 (\beta_n h)] \} \cos n\omega (\tau - \tau_n) + \sum_{n=1}^{\infty} \frac{B_n [X (\beta_n z) X (\beta_n h) + Y (\beta_n z) Y (\beta_n h)]}{X^2 (\beta_n h) + Y^2 (\beta_n h)} \sin n\omega (\tau - \tau_n)
\end{aligned}$$

$$+\sum_{n=1}^{\infty}\frac{B_n\left[Y(\beta_n z)\,X(\beta_n h)-X(\beta_n z)\,Y(\beta_n h)\right]}{X^2(\beta_n h)+Y^2(\beta_n h)}\cos n\omega(\tau-\tau_n)$$

$$-\sum_{n=1}^{\infty}\frac{2(q_m-q_0)\sin\mu_k\dfrac{h-z}{h}\cos\mu_k}{\mu_k-\sin\mu_k\cdot\cos\mu_k}\exp\left(-\frac{D\mu_k^2}{h^2}\tau\right)$$

$$-\frac{\chi_0}{1+\varkappa h}\sum_{n=1}^{\infty}\sum_{k=1}^{\infty}\frac{2A_n\alpha' Dn\omega\sin\mu_k\sin\mu_k\dfrac{h-z}{h}}{h\left[\left(\dfrac{D\mu_k^2}{h^2}\right)^2+n^2\omega^2\right]\left(1+\dfrac{1}{\alpha' h}\cos^2\mu_k\right)}\exp\left(-\frac{D\mu_k^2}{h^2}(\tau-\tau_n)\right), \tag{6}$$

where

$$\beta_n=\sqrt{\frac{n\omega}{D}};\quad \alpha'=\frac{\alpha}{D};\quad X(\beta_n z)=\operatorname{sh}\beta_n z\cos\beta_n z$$

$$+\frac{\beta_n}{\alpha'}(\operatorname{ch}\beta_n z\cos\beta_n z-\operatorname{sh}\beta_n z\sin\beta_n z);\quad Y(\beta_n z)=\operatorname{ch}\beta_n z\sin\beta_n z+\frac{\beta_n}{\alpha'}(\operatorname{ch}\beta_n z\cos\beta_n z+\operatorname{sh}\beta_n z\sin\beta_n z),$$

μ_k are the roots of the characteristic equation, $\tan\mu=-(1/\alpha' h)\mu$, $\mu=i\sqrt{(p/D)}h$; p is a parameter of the operational method.

The solution (6) obtained described the density field of vapors contained in the pores of the dry soil layer. It the temperature variation is repeated regularly, a periodically varying mode of mass transfer practically independent of the initial condition is established in the dry soil in the course of time. In a mode of steady-state diffusion the last two terms of solution (6) are equal to zero.

From (6) we can find the density of the diffusion vapor flow (j) through the soil surface (z = 0) and thereby obtain the important formula explaining the temporal (diurnal) variation of evaporation of water from the soil.

The expression for the density of the diffusion vapor flow contains the dimensionless complex $\beta_n h$, which is, as is easy to substantiate, a small quantity. Actually, investigations [16, 17] have established that the regular diurnal variation of temperature on the surface and in the depth of the soil is approximated sufficiently well by the first two harmonics (n = 1, 2) of the Fourier series. The thickness of the dry soil layer is usually several centimeters. Only in the desert zone can it prove to be more than 10 cm. If we use h = 1 cm, D = 0.11 cm^2/sec, and T = 86,400 sec, for harmonic n = 1, which mainly determines the variation of evaporation of water from soil, we obtain

$$\beta_n h=\sqrt{\frac{2\pi n}{DT}}h=\sqrt{\frac{6.28}{0.11\cdot 86400}}=2.57\cdot 10^{-2}.$$

If we simplify the expression for the density of the steady-state diffusion vapor flow on the basis that $\beta_n h$ is a small quantity, we obtain the formula of the diurnal variation of evaporation of soil water, which after a certain transformation reduces to a quite simple form

$$j(0,\tau)=D\frac{q_s(h,\tau)-q_a}{h+\dfrac{1}{\alpha'}}+\frac{\chi_0 h^2}{\left(h+\dfrac{1}{\alpha'}\right)(1+\varkappa h)}\cdot\frac{\partial t(0,\tau)}{\partial\tau}. \tag{7}$$

The temporal (diurnal) variation of evaporation of water from the soil according to Eq. (7) represents the superposition of the diffusion flow of vapors passing through the dry layer from the depth of the soil (first term of the formula) and the vapors formed or absorbed within the dry layer upon a change of soil temperature (second term of the formula). In other words, in the stage of heating of the soil ($\partial t/\partial\tau > 0$) the vapors formed within the dry soil layer as a consequence of desorption are added to the vapors formed in the region of moist soil (in the evaporation zone [7]) and diffusing through the dry layer. In the stage of decrease of temperature ($\partial t/\partial\tau < 0$) sorption of vapors, arriving mainly from the depth of the soil and under certain conditions from the ground air, occurs in the dry soil layer. In the presence of a vegetation cover on the soil surface, the evaporation of plants (transpiration) is added to the physical evaporation determined by Eq. (7).

By means of Eq. (7) which is distinguished by simplicity, the variation of evaporation of water from soil is described by quantities easily determined by experiment. It follows from this formula that physical evaporation of soil water depends on the humidity of the ground air, wind speed (in terms of the mass-transfer coefficient), and especially on the variation of temperature and thickness of the dry layer of soil, as well as on the thermal and sorption properties of the soil.

The character of the dependence of evaporation on the thickness of the dry soil layer is easy to perceive directly from Eq. (7). The variation of evaporation in the case of a small thickness of the dry layer, according to Eq. (7) is determined mainly by the diffusion flow of vapors passing through the dry layer from the depth of the soil, and in the case of a considerable thickness h by vapor desorption and sorption processes occurring within the dry soil layer. If we assume that the mass-transfer coefficient (α) in the first approximation depends on the wind speed according to a linear law, then when $h = 0$ Eq. (7) is converted to the empirical formula of evaporation from an open water surface known in meteorology [2, 3].

By means of Eq. (7) it is easy to calculate (by integration) the total evaporation of water from soil during a 24 h period. If the variation of temperature on the soil surface is approximated by a periodic function, the integral of the second term of Eq. (7) during the period will be equal to zero. Hence it follows that the desorption and sorption processes occurring in the hygroscopic region of soil in the case of a periodic change of temperature do not affect the quantity of diurnal evaporation, which depends mainly on the rate of the diffusion transfer of vapors through the dry soil layer, taken into account by the first term of Eq. (7). The independence of the total diurnal evaporation from the desorption and sorption processes occurring in the case of a periodic change of temperature in the hygroscopic region of soil is explained in that the mass of vapors formed within the dry layer in the heating stage is equal to the mass of vapors absorbed in this same layer in the cooling stage of the soil. Thus, as a result of desorption and sorption processes, in a 24 h period in the dry soil layer there occurs moisture circulation, which, although it affects considerably the temporal variation of evaporation, does not affect the quantity of total evaporation of water from the soil during a 24 h period.

NOTATION

q	is the vapor density (state parameter of vapor);
z, τ	are the coordinate and the time;
q_a	is the vapor density in the ground layer of air;
h	is the thickness of the dried layer of soil;
$q_s(h, \tau)$	is the density of the saturating vapors at the soil temperature at level $z = h$;
q_m	is the density of vapors in equilibrium with moisture in soil equal to maximum hygroscopicity;
D	is the coefficient of diffusion of water vapors in the soil;
$w(z, \tau)$	is the specific power of vapor sources acting within the dry soil layer;
$\chi_0, \varkappa$	are constants characterizing the specific power of the internal sources;
α	is the mass-transfer (vapor-transfer) coefficient;
t	is the temperature of the soil surface;
t_0	is the average temperature of the soil surface;
A_n, τ_n	are the amplitude and phase of the n-th harmonic of the Fourier series representing the diurnal variation of the temperature on the soil surface;
B_n	is the amplitude of the n-th harmonic of the Fourier series representing the function $q_s(h, \tau)$;
ω	is the frequency corresponding to the 24 h period (T);
$j(0, \tau)$	is the vapor flow density at $z = 0$.

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