



# A Phenomenological Model of the Increase in Solute Concentration in Ground Water Due to Evaporation

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**Abstract.** We present a new phenomenological model of the evaporation of ground water containing a polluting material in the dissolved form. Only the one-dimensional case is treated. It is assumed that there exists a sharp evaporation front separating between the dry and the water-saturated soil. The water-saturated soil is assumed to occupy a semi-infinite domain  $x > X(t)$ , where  $x$  is a vertical coordinate directed downward and  $X(t)$  is a position of the evaporation front. The mathematical description is based on four linear diffusion equations coupled through four boundary conditions, one of which is nonlinear, on the free moving evaporation front. We use a similarity solution of the governing equations and analyze it qualitatively showing that the solute concentration increases in the upward vertical direction and reaches its maximum on the evaporation front. The dependence of the solute concentration at the evaporation front and of the velocity of the front on the initial solute concentration and the temperature of the ground surface are computed. It is shown that for not high values of the initial solute concentration that are below the concentration value  $c_d$  at which a deposition of the pollutant sets in, the solute concentration on the evaporation front can reach values that are above the deposition value  $c_d$ . These results point to a possible mechanism of pollutant deposition in ground water caused by the evaporation.

**Key words:** polluted ground water, evaporation, mathematical model, vertical pollutant redistribution, pollutant deposition.

## Nomenclature

### *Latin symbols*

$a$	thermal diffusivity [ $\text{m}^2 \text{s}^{-1}$ ].
$c$	solute concentration [1].
$C$	specific heat at constant pressure [ $\text{J K}^{-1} \text{kg}^{-1}$ ].
$D$	diffusion coefficient [ $\text{m}^2 \text{s}^{-1}$ ].
$h$	enthalpy [ $\text{J kg}^{-1}$ ].
$m$	porosity [1].
$P$	pressure [Pa].

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$q$	specific heat of phase transition [ $\text{J kg}^{-1}$ ].
$Q_c$	diffusive flux density of mass of salt [ $\text{m s}^{-1}$ ].
$Q_v$	diffusive flux of mass of vapor [ $\text{kg m}^{-2} \text{s}^{-1}$ ].
$Q_T$	diffusive flux of heat [ $\text{J m}^{-2} \text{s}^{-1}$ ].
$R$	gas constant [ $\text{J kg}^{-1} \text{K}^{-1}$ ].
$t$	time [s].
$T$	temperature [K].
$V$	velocity of the evaporation front [ $\text{m s}^{-1}$ ].
$x$	vertical coordinate [m].
$X$	position of the evaporation front [m].

*Greek symbols*

$\alpha$	coefficient [K].
$\beta$	value of the similarity variable $\xi$ at the evaporation front [ $\text{m s}^{-1/2}$ ].
$\gamma$	dimensionless similarity coordinate of the evaporation front [1].
$\lambda$	thermal conductivity [ $\text{W m}^{-1} \text{K}^{-1}$ ].
$\nu$	vapor concentration in air [1].
$\xi$	similarity variable [ $\text{m s}^{-1/2}$ ].
$\rho$	density [ $\text{kg m}^{-3}$ ].

*Subscripts*

a	air.
c	solute.
m	mixture.
s	skeleton of porous medium.
$T$	temperature.
v	vapor.
w	water.
0	initial value.
+	right ahead of the evaporation front in the water saturated domain.
-	right behind the evaporation front in the air-vapor domain.
*	at the evaporation front.

*Superscript*

0	boundary value on the ground surface $x = 0$ .
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**1. Introduction**

The growing demand for understanding and treating the process of soil contamination caused by pollutants dissolved in ground water has inspired an increased interest in recent years to the problems of evolution of polluting admixtures. An adequate mathematical description of the process presents a considerable challenge due to the fact that a porous soil saturated with air and contaminated water is a rather complicated multiphase system. Transfer processes in such a system are influenced by a variety of physical and chemical factors that have to be properly accounted for. One of such processes is the evaporation of ground water.

Basically, there are two different approaches to the description of transfer processes in porous media. The first approach is mechanistic. It is based on determining experimentally, for every given physical situation, functions and coefficients

appearing in semi-empirical equations that govern a particular transfer process. Such an approach is used, for instance, in the works of Phillip and De Vries (1957); Whitaker (1977); De Vries (1987); Sophocleous (1979); Melayah *et al.* (1996). There exists a considerable amount of literature in the framework of this approach dealing with a great variety of transfer phenomena in porous media. Restricting ourselves to the process of evaporation within a porous soil, which is a subject of the present paper, we cite here just some of the works on this topic that appeared recently (Fischer *et al.*, 1996; Lewan and Jansson, 1996; Yakirevich *et al.*, 1997; Yamanaka *et al.*, 1997).

The second approach consists in using the basic conservation laws in the framework of mechanics of multi-phase media and the laws of classical thermodynamics for describing the dynamics in a porous medium. This approach is, for instance, traditionally used in problems related to the oil, gas and heat recovery from natural reservoirs that are porous media (Scheidegger, 1974; Nigmatulin, 1987, pp. 294–330; O’Sullivan, 1985), and in recent times it was extended to problems of the soil science of a more general nature (Helmig, 1997, pp. 85–140). A consideration based on the conservation laws applied in this approach can render a mathematical description of the problem too complex and, as a consequence, analytically intractable. This has stimulated a development of numerical tools and a use of high-speed computers for treating multi-phase transport processes in porous media whose description is based on the first principles, see Helmig (1997), Chapters 4–6, for recent results and a review. At the same time, from the mathematical standpoint, treating simple realistic physical situations for which there exist solutions in a closed analytical form is also quite useful within this approach because it provides one with a clear qualitative picture of the phenomena studied and gives a precise description of the physical quantities within a mathematical model used.

In the present paper, we use the second approach for the formulation and analysis of a phenomenological model of the evaporation of ground water containing a pollutant in the dissolved form. The analysis reduces to a treatment of four linear diffusion equations that are coupled through a set of boundary conditions on the moving evaporation front. One of these conditions is strongly nonlinear. It is shown that the evaporation produces a gradient directed upward of the solute concentration in all cases considered. Let  $c_d$  denote the solubility, i.e., the concentration value at which a deposition of the pollutant sets in. We have shown that for initial values of the solute concentration that are well below the value of  $c_d$  the concentration on the evaporation front can reach values that are considerably greater than  $c_d$ .

The paper is organized as follows. In Section 2, a new phenomenological mathematical model of the evaporation of polluted ground water in the one-dimensional case is presented and an initial-boundary-value problem describing the evaporation process is formulated. An analytical treatment of the problem by means of a similarity solution approach is given in Section 3. The problem is reduced to a transcendental equation. Results of a numerical treatment of this equation are presented

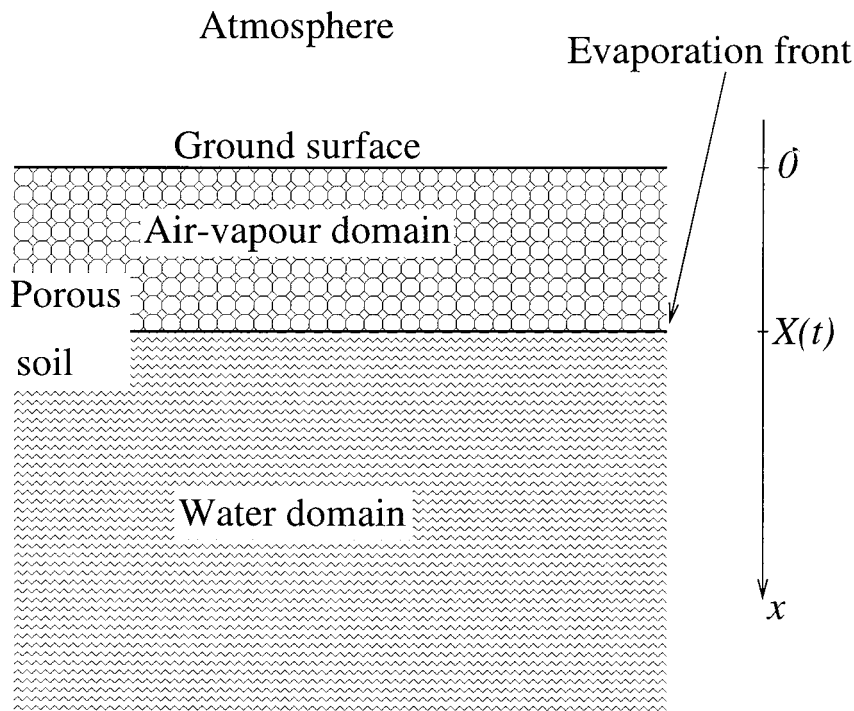


Figure 1. Schematics of the model geometry.

in Section 4. Finally, in Section 5, conclusions are made and the environmental applicability of the analysis is discussed.

## 2. Model Formulation

We consider the process of evaporation of ground water containing a pollutant in the dissolved form in the geometric configurations as shown in Figure 1. The soil is assumed to be a porous medium of constant porosity containing a semi-infinite domain saturated with polluted water. A uniform initial concentration of the solute and temperature are prescribed. The atmosphere and the soil are treated as two physical systems that interact on the ground surface where an exchange of mass and energy occurs. It is assumed that the soil does not affect the state of the atmosphere. The latter is characterized by two constant parameters: the relative humidity and the temperature.

Experiments show (Melayah *et al.*, 1996; Yakirevich *et al.*, 1997) that the evaporation process in a soil containing a water saturated domain leads to the formation of a narrow layer-like zone which separates the domain of pores dominated by water from the air-vapor dominated domain. This zone is characterized by a sharp gradient of the water content in the direction transverse to the layer shaped extension of the zone. We shall model this zone as a sharp front of evaporation

and formulate the problems as a Stefan like problem. We treat the evaporation process of water in the motionless state and are particularly interested in analyzing a vertical redistribution of the solute concentration as a result of the evaporation. Only the one-dimensional case is considered.

The origin of the coordinate system is located on the ground surface and the vertical  $x$ -axis is directed downwards parallel to the gravity field. The domain  $0 < x < X(t)$  inside the porous soil is assumed to be filled with an air-vapor mixture, where  $X(t)$  is a location of the moving evaporation front as a function of time  $t$ . At  $x = 0$ , there is a physical contact with the atmosphere. The whole half-space  $x \geq X(t)$  inside the porous soil is assumed to be occupied by water containing a salt in the dissolved form. We will call the domain filled with an air-vapor mixture also the vapor domain.

The evaporation occurs because the partial pressure of water vapor in the air above the ground is assumed to be lower than the partial pressure of the saturated vapor. On the evaporation front the concentration of water vapor corresponds to the saturation pressure and it is generally higher than the vapor concentration on the ground surface. Under these conditions, a diffusion transfer process of vapor will take place in the air-vapor filled soil domain. One can show by using the law relating the evaporation pressure to the temperature that, under atmospheric conditions, the partial pressure and the density of water vapor are considerably smaller than the partial pressure and the density of air, respectively. The density of air-vapor mixture can be assumed to be approximately equal to the density of air. Air and water vapor are treated as ideal gases. The term water will be used throughout to denote water containing a polluting substance in the dissolved form. We neglect the advection in air-vapor mixture.

In the domain of air-vapor mixture the governing equations, i.e., the mass and energy conservation laws, and the equations of state, read

$$\begin{aligned} \frac{\partial}{\partial t}(m\rho_v) + \frac{\partial}{\partial x}Q_v &= 0, & (\rho C)_- \frac{\partial T}{\partial t} + \frac{\partial}{\partial x}Q_T &= 0, \\ P_v &= \rho_v R_v T, & P_a &= \rho_a R_a T, & \text{with} \\ Q_v &= -m D_v \frac{\partial \rho_v}{\partial x} & \text{and} & Q_T = -\lambda_- \frac{\partial T}{\partial x}. \end{aligned} \quad (1)$$

It is assumed that the soil porosity  $m$ , the density of the solid skeleton of soil  $\rho_s$ , and the density of air  $\rho_a$  are constant. In (1),

$$(\rho C)_- = m\rho_m C_m + (1 - m)\rho_s C_s \quad \text{and} \quad \lambda_- = m\lambda_m + (1 - m)\lambda_s. \quad (2)$$

In the domain saturated with water containing a pollutant the governing equations, i.e., the conservation of mass for the salt, and the conservation of energy are given by

$$\frac{\partial}{\partial t}(mc) + \frac{\partial}{\partial x}Q_c = 0, \quad (\rho C)_+ \frac{\partial T}{\partial t} + \frac{\partial}{\partial x}Q_T = 0, \quad (3)$$

with

$$Q_c = -m D_c \frac{\partial c}{\partial x}, \quad Q_T = -\lambda_+ \frac{\partial T}{\partial x},$$

where

$$(\rho C)_+ = m\rho_w C_w + (1-m)\rho_s C_s \quad \text{and} \quad \lambda_+ = m\lambda_w + (1-m)\lambda_s. \quad (4)$$

It is assumed that the variations of the density of water  $\rho_w$  can be neglected.

On the moving evaporation boundary between water and air–vapor mixture there are three boundary conditions – the conservation of mass for  $H_2O$ , the conservation of mass for the pollutant, and the conservation of energy – which are as follows:

$$[m\rho V - Q_v] = 0, \quad [m\rho c V - Q_c] = 0, \quad [m\rho h V - Q_T] = 0. \quad (5)$$

Here  $[f]$  is the jump of the variable  $f$  across the boundary  $x = X(t)$ , and  $V$  is the velocity of the evaporation front.

On the evaporation boundary the thermodynamic conditions of an equilibrium phase transition must be satisfied. These conditions read

$$T_+ = T_- = T_*, \quad P_+ = P_- = P_*, \quad (6)$$

where  $P_+ = P_w$  and  $P_- = P_a + P_v$ . Conditions (6) allow us to use an explicit dependence of the partial vapor pressure on the temperature and the solute concentration at the evaporation boundary as follows (Vukalovitch, 1955, p. 10; Rabinovich and Khavin, 1977, p. 266):

$$P_{v-} = F(T_* - \alpha c_+),$$

where

$$F(z) = 10^5 \exp \left[ -7226.6 \left( \frac{1}{z} - \frac{1}{373.16} \right) + 8.2 \ln \frac{373.16}{z} - 0.0057(373.16 - z) \right]. \quad (7)$$

We assume that  $D_v$ ,  $D_c$ ,  $\lambda_-$ ,  $\lambda_+$ ,  $(\rho C)_-$  and  $(\rho C)_+$  are constant.

The conservation of mass for vapor, i.e., the first of (1), takes the form of a diffusion equation

$$\frac{\partial v}{\partial t} = D_v \frac{\partial^2 v}{\partial x^2}, \quad 0 < x < X(t), \quad t > 0, \quad (8)$$

where  $v = \rho_v/\rho_a$  is the vapor concentration; and the conservation of energy in the domain of air–vapor mixture, i.e., the second of (1), is

$$\frac{\partial T}{\partial t} = a_- \frac{\partial^2 T}{\partial x^2}, \quad 0 < x < X(t), \quad t > 0, \quad (9)$$

with

$$a_- = \frac{\lambda_-}{(\rho C)_-}. \quad (10)$$

Similarly, the conservation of mass for the salt in water, i.e., the first of (3), is given by

$$\frac{\partial c}{\partial t} = D_c \frac{\partial^2 c}{\partial x^2}, \quad x > X(t), \quad t > 0; \quad (11)$$

and the conservation of energy in the water domain, i.e., the second of (3), reads

$$\frac{\partial T}{\partial t} = a_+ \frac{\partial^2 T}{\partial x^2}, \quad x > X(t), \quad t > 0, \quad (12)$$

where

$$a_+ = \frac{\lambda_+}{(\rho C)_+}. \quad (13)$$

The Equations (8), (9), (11), (12) are linked to one another through the boundary conditions on the evaporation front.

The conservation of mass for H<sub>2</sub>O on the moving evaporation boundary  $x = X(t)$  in the absence of motion of the media takes the form

$$\frac{\rho_w - \rho_v}{\rho_a} V = D_v \frac{\partial v}{\partial x}, \quad \text{at } x = X(t). \quad (14)$$

Since  $\rho_w \gg \rho_v$ ,  $\rho_v$  in (14) can be neglected to give

$$\frac{\rho_w}{\rho_a} V = D_v \frac{\partial v}{\partial x}, \quad \text{at } x = X(t). \quad (15)$$

The conservation of mass for the salt on the evaporation boundary is

$$c_+ V + D_c \left( \frac{\partial c}{\partial x} \right)_+ = 0, \quad \text{at } x = X(t), \quad (16)$$

and the energy balance on the boundary can be written as

$$\begin{aligned} m D_v \rho_a h_w \left( \frac{\partial v}{\partial x} \right)_+ - \lambda_- \left( \frac{\partial T}{\partial x} \right)_- + \\ + \lambda_+ \left( \frac{\partial T}{\partial x} \right)_+ = m \rho_v q V, \quad \text{at } x = X(t), \end{aligned} \quad (17)$$

where  $q = h_v - h_w$  is the specific heat of phase transition.

An order of magnitude evaluation of the terms in (17) can be carried out as follows. Let  $\delta \rho_v$  and  $\delta T$  denote the characteristic spatial variations of  $\rho_v$  and  $T$ ,

respectively, on the characteristic length scales  $\delta x_\rho$  and  $\delta x_T$ , respectively. By using (15) we can express the term on the right hand side of (17) as

$$m\rho_v q V = m\rho_v q \frac{\rho_a}{\rho_w} D_v \left( \frac{\partial v}{\partial x} \right)_- = m(h_v - h_w) D_v \frac{\rho_v}{\rho_w} \left( \frac{\partial \rho_v}{\partial x} \right)_-. \quad (18)$$

The first term on the left hand side of (17) can be written as

$$m D_v \rho_a h_w \left( \frac{\partial v}{\partial x} \right)_- = m h_w D_v \left( \frac{\partial \rho_v}{\partial x} \right)_-. \quad (19)$$

For the dimensional values, with dimensions indicated in the Nomenclature, it holds typically that  $h_v = O(10^6)$ ,  $h_w = O(10^5)$ ,  $D_v = O(3 \times 10^{-5})$ , and  $\rho_v/\rho_w = O(10^{-4})$ . The latter estimate follows from  $\rho_w = 10^3$  and the estimate  $\rho_v = O(10^{-1})$ . The order of magnitude of  $\rho_v$  is estimated by noting that  $\rho_v$  attains its maximum on the evaporation front. Hence, by using (7) we can write

$$\rho_v|_{x=X(t)} = \left( \frac{P_v}{RT} \right)_{|x=X(t)} \leq \frac{1}{R} \max_T \frac{F(T)}{T} = \frac{1}{461} \frac{20000}{335} = 0.13, \quad (20)$$

where the temperature  $T$  is assumed to be in the range  $T \in [273, 335]$ . Since  $m = 0.25$ , as an estimate of the order of magnitude of the term on the right hand side of (17) given by (18) can be taken

$$10^{-3} O \left( \frac{\delta \rho_v}{\delta x_\rho} \right). \quad (21)$$

The order of magnitude of the first term on the left hand side of (17) given by (19) is estimated as

$$O \left( \frac{\delta \rho_v}{\delta x_\rho} \right). \quad (22)$$

The thermal diffusion terms in (17) can be estimated as

$$\lambda_- \left( \frac{\partial T}{\partial x} \right)_-, \lambda_+ \left( \frac{\partial T}{\partial x} \right)_+ = O \left( \frac{\delta T}{\delta x_T} \right), \quad (23)$$

because, for the dimensional values, typically we have  $\lambda_+ = O(1)$  and  $\lambda_- = O(1)$ . Since  $\delta x_\rho$  and  $\delta x_T$  are of the same order of magnitude, say  $\delta L$ , and since typically  $\delta \rho_v = O(10^{-1})$ , and  $\delta T = O(10)$ , we have

$$O \left( \frac{\delta \rho_v}{\delta x_\rho} \right) = O \left( \frac{10^{-1}}{\delta L} \right) \quad \text{and} \quad O \left( \frac{\delta T}{\delta x_T} \right) = O \left( \frac{10}{\delta L} \right). \quad (24)$$

Therefore,

$$O \left( \frac{\delta \rho_v}{\delta x_\rho} \right) < O \left( \frac{\delta T}{\delta x_T} \right). \quad (25)$$

The inequality (25), together with the above estimates of the terms in (17), imply that the transfer of energy related to the vapor diffusion (the first term on the left hand side of (17)) and the absorption of energy on the evaporation front (the term on the right hand side of (17)) are both negligible compared to the second and third terms on the left hand side of (17) representing the heat conduction. Hence, we neglect the diffusion and absorption terms in (17) and write the energy balance on the evaporation front as

$$\lambda_- \left( \frac{\partial T}{\partial x} \right)_- = \lambda_+ \left( \frac{\partial T}{\partial x} \right)_+, \quad \text{at } x = X(t). \quad (26)$$

Since  $v = \rho_v/\rho_a = (R_a P_v)/(R_v P_a)$ , condition (7) can be expressed as

$$v_- = \frac{R_a F(T_* - \alpha c_+)}{R_v P_a}, \quad \text{at } x = X(t). \quad (27)$$

Equations (15), (16), (26) and (27) give the full set of conditions on the moving boundary  $x = X(t)$ . The first three of them are linear in the unknown dependent variables, but the condition (27) is nonlinear, since the function  $F(z)$  given by (7) depends nonlinearly on  $z$ . At the initial instant, the solute concentration and the temperature in the water domain are prescribed as

$$c = c_0, \quad T = T_0, \quad \text{for } t = 0, \quad x \geq X(0), \quad (28)$$

where  $c_0$  and  $T_0$  are independent of  $x$ . Also, on the ground surface the air humidity and the temperature are prescribed as

$$v = v^0, \quad T = T^0, \quad \text{at } x = 0, \quad \text{for } t \geq 0, \quad (29)$$

where  $v^0$  and  $T^0$  do not depend on time. For each fixed  $t$ , the solute concentration and the temperature at infinity of the water domain are assumed to be equal to their respective values at the initial instant

$$\lim_{x \rightarrow \infty} c(x, t) = c_0, \quad \lim_{x \rightarrow \infty} T(x, t) = T_0. \quad (30)$$

In the next sections we solve the system of Equations (8), (9), (11), (12) subject to the initial conditions (28), the boundary conditions on the unknown moving evaporation front (15), (16), (26) and (27), and the boundary conditions (29) and (30) on the ground surface and at infinity of the water domain, respectively.

### 3. Similarity Solution

The problem (8), (9), (11), (12), (15), (16), (26)–(30) possesses a similarity solution that describes the propagation of a plane evaporation front through a water saturated soil. It is obtained in a standard manner. We introduce a similarity variable

$$\xi = \frac{x}{\sqrt{t}} \quad (31)$$

and look for a solution of the problem in the form

$$v = v(\xi), \quad T = T(\xi), \quad c = c(\xi), \quad X(t) = \beta\sqrt{t}. \quad (32)$$

Substitution of  $v = v(\xi)$  into Equation (8), and use of the boundary conditions  $v = v^0$  at  $x = 0$ , and  $v = v_-$  at  $x = X(t)$  result in a two-point boundary-value problem for  $v(\xi)$

$$\begin{aligned} D_v v''(\xi) + \frac{\xi}{2} v'(\xi) &= 0, \\ v &= v^0, \quad \text{at } \xi = 0, \quad v = v_-, \quad \text{at } \xi = \beta, \end{aligned} \quad (33)$$

where the prime denotes  $d/d\xi$ . Integration of (33) gives

$$v = v^0 + (v_- - v^0) \frac{\operatorname{erf}\left(\frac{\xi}{2\sqrt{D_v}}\right)}{\operatorname{erf}\left(\frac{\beta}{2\sqrt{D_v}}\right)}, \quad 0 < x < X(t), \quad t > 0, \quad (34)$$

where

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-s^2} ds \quad (35)$$

is the error function. Similarly, a solution of Equation (9) that satisfies the boundary conditions  $T = T^0$  at  $x = 0$ , and  $T = T_*$  at  $x = X(t)$  can be written as

$$T_v = T^0 + (T_* - T^0) \frac{\operatorname{erf}\left(\frac{\xi}{2\sqrt{a_-}}\right)}{\operatorname{erf}\left(\frac{\beta}{2\sqrt{a_-}}\right)}, \quad 0 < x < X(t), \quad t > 0. \quad (36)$$

Equations (34) and (36) give the distributions of the vapor concentration and temperature, respectively.

For the water domain  $x > X(t)$ , solutions of Equations (11) and (12) giving the solute concentration and the temperature, respectively, that satisfy the corresponding boundary conditions (30) at infinity and the conditions  $c = c_+$ ,  $T = T_*$  on the evaporation front  $x = X(t)$ , are

$$c = c_0 + (c_+ - c_0) \frac{\operatorname{erfc}\left(\frac{\xi}{2\sqrt{D_c}}\right)}{\operatorname{erfc}\left(\frac{\beta}{2\sqrt{D_c}}\right)}, \quad x > X(t), \quad t > 0, \quad (37)$$

and

$$T_w = T_0 + (T_* - T_0) \frac{\operatorname{erfc}\left(\frac{\xi}{2\sqrt{a_+}}\right)}{\operatorname{erfc}\left(\frac{\beta}{2\sqrt{a_+}}\right)}, \quad x > X(t), \quad t > 0, \quad (38)$$

where

$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z). \quad (39)$$

In (36) and (38) we use the subscripts v and w in order to distinguish between the temperature distributions in the vapor domain  $T_v$  and in the water domain  $T_w$ . The solution (34), (36)–(38) contains four unknown constants  $v_-$ ,  $T_*$ ,  $c_+$  and  $\beta$ . For determining these constants, four boundary conditions on the evaporation front (15), (16), (26) and (27) will be used.

We introduce the notation  $\gamma = \beta/(2\sqrt{D_v})$ . From (32), the velocity of the evaporation front is given by  $V = \beta/(2\sqrt{t}) = \gamma\sqrt{D_v}/\sqrt{t}$ . By using the solution  $v$ ,  $T_v$ ,  $c$  and  $T_w$  given by (34), (36)–(38), and the above expressions for  $\beta$  and  $V$  in the boundary conditions (15), (16) and (26) the conditions are expressed as

$$\begin{aligned} \sqrt{\pi} \frac{\rho_w}{\rho_a} \gamma &= (v_- - v^0) \frac{e^{-\gamma^2}}{\operatorname{erf}(\gamma)}, \\ \sqrt{\pi} \frac{D_v}{D_c} c_+ \gamma &= (c_+ - c_0) \frac{e^{-\gamma^2 D_v/D_c}}{\operatorname{erfc}(\gamma\sqrt{D_v/D_c})}, \quad \text{and} \\ \frac{\lambda_- \sqrt{a_+} T_* - T^0}{\lambda_+ \sqrt{a_-} T_0} \frac{1}{\operatorname{erf}(\gamma\sqrt{D_v/a_-})} &= \left(1 - \frac{T_*}{T_0}\right) \frac{e^{-\gamma^2 D_v(1/a_+ - 1/a_-)}}{\operatorname{erfc}(\gamma\sqrt{D_v/a_+})}, \end{aligned} \quad (40)$$

respectively. From (40),  $v_-$ ,  $c_+$  and  $T_*$  can be written explicitly as functions of  $\gamma$

$$\begin{aligned} v_-(\gamma) &= \sqrt{\pi} \frac{\rho_w}{\rho_a} \gamma \operatorname{erf}(\gamma) e^{\gamma^2} + v^0, \\ c_+(\gamma) &= \frac{c_0 e^{-\gamma^2 D_v/D_c}}{e^{-\gamma^2 D_v/D_c} - \sqrt{\pi} D_v/D_c \gamma \operatorname{erfc}(\gamma\sqrt{D_v/D_c})}, \\ T_*(\gamma) &= \frac{T^0 A(\gamma) + T_0 B(\gamma)}{A(\gamma) + B(\gamma)}, \end{aligned} \quad (41)$$

where in the third of (41)

$$A(\gamma) = \frac{\lambda_- \sqrt{a_+}}{\lambda_+ \sqrt{a_-}} \frac{1}{\operatorname{erf}(\gamma\sqrt{D_v/a_-})} \quad \text{and} \quad B(\gamma) = \frac{e^{-\gamma^2 D_v(1/a_+ - 1/a_-)}}{\operatorname{erfc}(\gamma\sqrt{D_v/a_+})}. \quad (42)$$

Substitution of the functions  $v_-(\gamma)$ ,  $c_+(\gamma)$  and  $T(\gamma)$  into the fourth boundary condition on the evaporation front (27) gives a single transcendental nonlinear equation for  $\gamma$  which we write as

$$v_-(\gamma) = \frac{R_a F(T_*(\gamma) - \alpha c_+(\gamma))}{R_v P_a}. \quad (43)$$

Both sides of Equation (43) are given explicitly as real-valued nonlinear functions of  $\gamma$ . Numerical solution of (43) was found by applying a standard mathematical software. Müller's method was used. For each combination of the physical

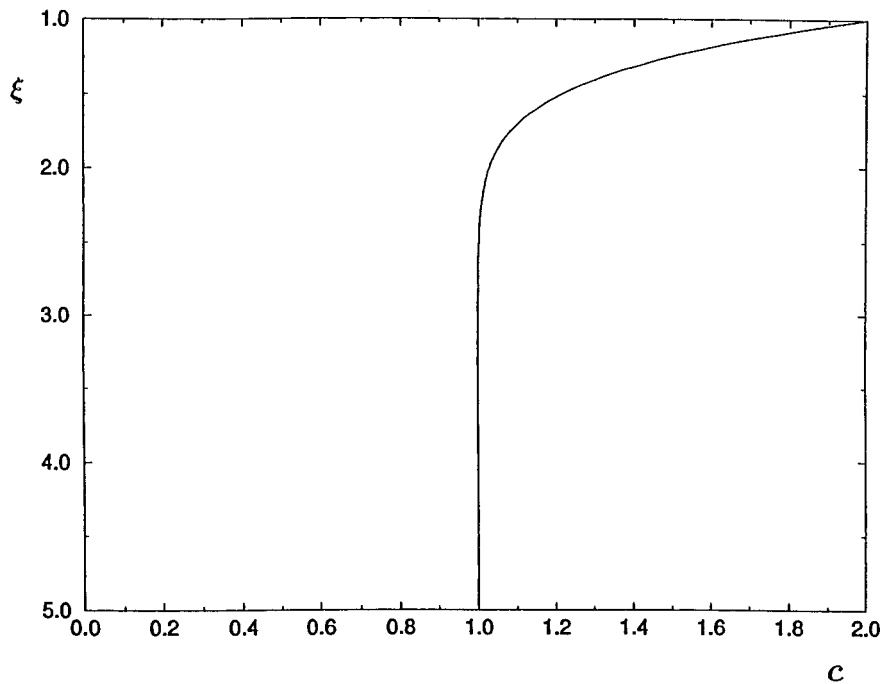


Figure 2. Solute concentration  $c$  as a function of the similarity variable  $\xi$ . The units are arbitrary.

parameters considered, our computations have shown that if Equation (43) has a positive solution then the solution is unique.

We show in the Appendix, by using the closed analytical form of (37) and of the second of (41) that as a result of the process of evaporation there appears a vertical distribution of the solute concentration in the ground water domain. At every fixed instant  $t$ , this distribution has a form of a monotonously decreasing function of  $x$  reaching its maximum  $c_+$  on the evaporation front. Figure 2 illustrates a typical distribution of the solute concentration with height in the water domain.

In the next section we present results of the numerical treatment of Equation (43).

#### 4. Numerical Results

Solutions of Equation (43) were found numerically for the following fixed values of the physical parameters:  $\rho_w = 10^3 \text{ kg m}^{-3}$ ,  $\rho_s = 2 \times 10^3 \text{ kg m}^{-3}$ ,  $R_a = 287 \text{ J kg}^{-1} \text{ K}^{-1}$ ,  $R_v = 461 \text{ J kg}^{-1} \text{ K}^{-1}$ ,  $P_a = 10^5 \text{ Pa}$ ,  $D_c = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $\alpha = 20 \text{ K}$ ,  $m = 0.25$ ,  $\lambda_w = 0.58 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\lambda_s = 2 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $C_w = 4.2 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ ,  $C_s = 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ . These values reflect a typical physical situation (Grigoriev, 1997, Chapters 9, 13, 15, 17). In particular, the porosity value of  $m = 0.25$  corresponds to that of a dense low porosity sand (Schelkachev and Lapuk, 1949, p. 55). The temperature in the water domain at the initial instant

was taken to be  $T_0 = 273.15 + 13$  K, i.e.,  $T_0 = 13^\circ\text{C}$ . Computations were performed for four representative values of air humidity on the ground surface: (i)  $\nu^0 = 0$ , the dry air case; (ii)  $\nu^0 = 0.002$ , a case of a slightly moist air; (iii)  $\nu^0 = 0.009$ , a moderately moist case; and (iv)  $\nu^0 = 0.018$ , a case of high moisture. The relative humidity  $H$  of a pollutant free air is given in percent by  $H = 100 P_v/P_{\text{sat}}(T)$ , where  $P_{\text{sat}}(T)$  is the saturation pressure at temperature  $T$ . Hence  $H = 100 P_v/F(T) = 100\rho_v R_v T/F(T) = 100\nu^0 \rho_a R_v T/F(T) = 100\nu^0 R_v P_a/(R_a F(T))$ . For instance, for  $T = 300$  K, we have  $F(T) = 3507.45$  Pa, and, therefore, in the cases at hand (i)  $H = 0$ , (ii)  $H = 9.16\%$ , (iii)  $H = 41.22\%$  and (iv)  $H = 82.44\%$ , for the values of  $R_a$ ,  $R_v$  and  $P_a$  given above, for the example of a pollutant free air. This explains the qualitative descriptions of the cases (i)–(iv) as dry, slightly moist, moderately moist and very moist, respectively.

For each  $T^0$ , we compute  $\rho_a = P_a/(R_a T^0)$  kg m<sup>-3</sup>,  $D_v = 2 \times 10^{-5} (T^0/273)^2$  m<sup>2</sup> s<sup>-1</sup>, the values of  $(\rho C)_-$  and  $\lambda_-$  given by (2), the values of  $(\rho C)_+$  and  $\lambda_+$  given by (4), and then the values of  $a_-$  and  $a_+$  defined by (10) and (13), respectively (Grigoriev, 1997, Chapter 17). The given and computed (for each  $T^0$ ) values of the physical parameters, together with a value of  $c_0$ , present a complete set of coefficients appearing in Equation (43), for each case (i)–(iv), see (41) and (42). Hence, for a given fixed pair  $(T^0, c_0)$ , all the coefficients in Equation (43) are determined in each case (i)–(iv).

For each set of the coefficients treated, we found numerically that Equation (43) has a unique solution. The solution was found by resorting to an IMSL routine ZREAL that uses Müller's method for locating roots of a real-valued function. For testing purposes, Equation (43) was also solved for several representative cases by using an equation solver from the XMAPLE program giving a complete agreement with the results obtained using the ZREAL routine. We performed computations for a dense set of values of temperature on the ground surface on the interval  $284 \text{ K} \leq T^0 \leq 340 \text{ K}$  and a dense set of values of solute concentration at the initial instant on the interval  $0 \leq c_0 \leq 0.36$ . In these computations, in each case (i)–(iv), the initial temperature in the water domain  $T_0$  and the air humidity on the ground surface  $\nu^0$  are fixed. The computed value of  $\gamma$  appears as a function of the ground surface temperature  $T^0$  and the initial solute concentration  $c_0$ , i.e.,  $\gamma = \gamma(T^0, c_0)$ . Hence, so is the solute concentration on the evaporation front  $c_+$  computed according to the second of (41), i.e.,  $c_+ = c_+(T^0, c_0)$ .

In Figure 3 elevation (or level) lines of the function  $c_+ = c_+(T^0, c_0)$ , i.e., the lines  $c_+(T^0, c_0) = \text{constant}$ , are shown in the rectangle  $(T^0, c_0) \in [284, 330] \times [0, 0.36]$ , for the dry air case, i.e.,  $\nu^0 = 0$ . The most conspicuous and physically significant feature seen in this figure is the increase of  $c_+(T^0, c_0)$ , as a function of temperature  $T^0$  on the ground surface, for a fixed initial concentration  $c_0$ . For instance, for the initial concentration of 0.17, the function  $c_+(T^0, 0.17)$  increases from its value of 0.267 for  $T^0 = 284$  to the value of 0.622 when  $T^0 = 330$ , see Table I.

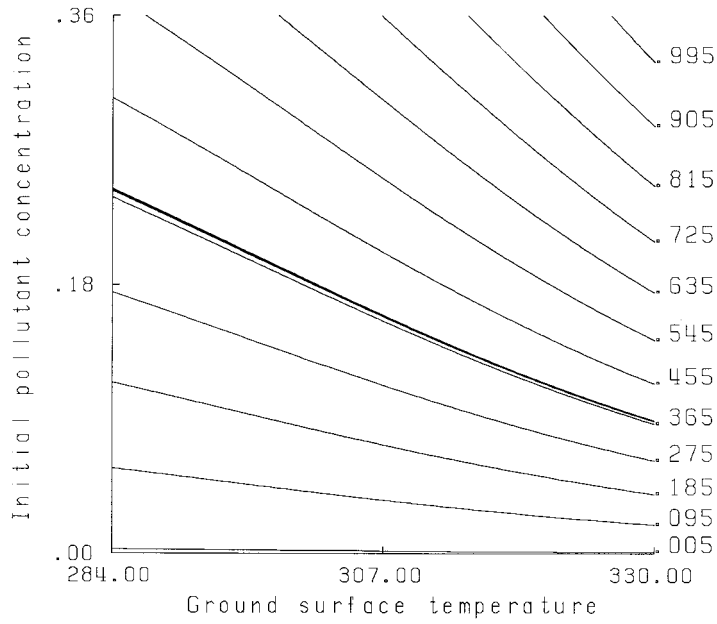


Figure 3. Elevation lines of the solute concentration on the evaporation front  $c_+ = c_+(T^0, c_0)$ , for the humidity on the ground surface  $v^0 = 0$ . The rest of the parameters are given in the text. The thick line is the elevation line for the elevation level  $c_+(T^0, c_0) = 0.372$ . For the domain of  $(T^0, c_0)$ , where  $c_+(T^0, c_0) > 0.372$ , a deposition of the pollutant on the evaporation front takes place.

Table I. Dependence of  $c_+(T^0, 0.17)$  on  $T^0$

$T^0$	$c_+(T^0, 0.17)$
284.0	0.267
288.8	0.287
293.7	0.310
298.5	0.337
303.4	0.368
308.2	0.403
313.1	0.443
317.9	0.487
322.7	0.537
327.6	0.592
330.0	0.622

Table II. Solubility  $c_d$  as a function of temperature  $T$  for NaCl aqueous solutions

Temperature $T$ (K)	Solubility $c_d$ (1)
273.15	0.357
293.15	0.359
313.15	0.364
333.15	0.372
353.15	0.381
373.15	0.394

The value  $0.267 = c_+(284, 0.17)$  is by the factor of 1.57 greater than the initial concentration value  $c_0 = 0.17$ , and  $0.622 = c_+(330, 0.17)$  is 3.6 times greater than 0.17. This means that even for moderate temperatures of air on the ground surface, there is a considerable increase of the maximum solute concentration attained on the evaporation front compared to the initial concentration. For high temperatures in the physically relevant range the increase is very strong. Also, for a fixed  $T^0$ , higher initial concentration values  $c_0$  result in higher values of the maximum concentration  $c_+$ .

Let  $c_d$  denote the solute concentration satisfying the following property: for  $c \leq c_d$  no deposition of the pollutant into the soil takes place, while when  $c > c_d$ , such a deposition occurs. The value of  $c_d$  called solubility is a function of temperature, i.e.,  $c_d = c_d(T)$ ; it depends on the chemical composition of each particular solute. We present here an example of the process of pollutant deposition as a result of the ground water evaporation by treating NaCl aqueous solutions. Table II shows the dependence of  $c_d$  on  $T$ , for NaCl aqueous solutions, for a discrete set of values of  $T$  (Rabinovich and Khavin, 1977, p. 86). We recall that in our computations, the solute temperature at the initial instant is equal to  $T_0 = 286.15$  K. From the third of (41) it follows that the temperature on the evaporation front  $T_*$  satisfies  $\min(T_0, T^0) \leq T_* \leq \max(T_0, T^0)$  because  $A(\gamma)$  and  $B(\gamma)$  in the third of (41) are positive, see (42), (2) and (4). Hence, for the range of temperature  $T^0$  in Figure 3, we have  $284 \text{ K} \leq T_* \leq 330 \text{ K}$ . From Table II it follows that in this range the solubility on the evaporation front satisfies  $c_d(T_*) \leq 0.372$ , for NaCl aqueous solutions.

In Figure 3 the elevation line of the elevation level  $c_+(T^0, c_0) = 0.372$  is drawn as a thick line. Since  $c_+ = c_+(T^0, c_0)$  grows both along the lines  $T^0 = \text{constant}$  and  $c_0 = \text{constant}$ , for every pair  $(T^0, c_0)$  that lies above the elevation line  $c_+(T^0, c_0) = 0.372$  the solute concentration on the evaporation front is greater than the solubility on the front implying that a deposition of the pollutant on the front takes place. We call the domain of  $(T^0, c_0)$  laying above the elevation line  $c_+(T^0, c_0) = 0.372$  in Figure 3 and in Figures 5, 7, and 9 presented in the sequel a deposition domain. Note that, for instance, in the case shown in Figure 3, for

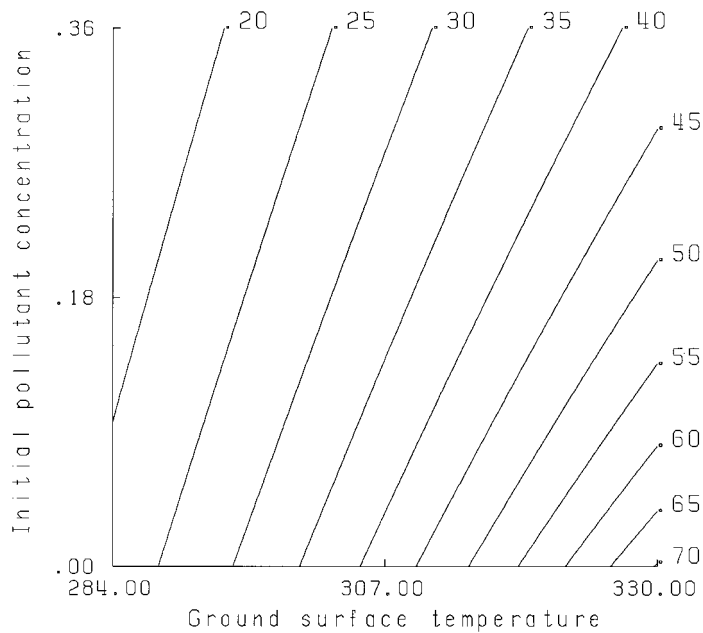


Figure 4. Elevation lines of the function  $\gamma = \gamma(T^0, c_0)$  characterizing the velocity of the evaporation front, for the humidity on the ground surface  $v^0 = 0$ . The rest of the parameters are given in the text. The gradient of  $\gamma(T^0, c_0)$  in the  $(T^0, c_0)$ -coordinates is roughly in the direction of the vector  $(1, -1)$ .

the initial solute concentration as low as  $c_0 = 0.095$ , the concentration on the evaporation front  $c_+(T^0, c_0)$ , for  $T^0 = 330$  K, is equal to 0.392, i.e., it is by the factor of 4 greater than  $c_0$  and, moreover, it is greater than the solubility at this temperature  $c_d(330) < 0.372$ , see Table II. This effect of a considerable increase, for large but realistic  $T^0$ , of the solute concentration on the front  $c_+(T^0, c_0)$  compared to the initial concentration  $c_0$  is present in all cases considered. It is caused by two factors which are (i) the monotonous increase, for a fixed  $T^0$ , of the concentration across the water domain from its value at infinity of the domain equal to  $c_0$  to the maximum value  $c_+(T^0, c_0)$  attained on the evaporation front, and (ii) the monotonous increase of  $c_+(T^0, c_0)$  as a function of  $T^0$  along each line  $c_0 = \text{constant}$ . The deposition domain in Figure 3 contains a subregion which is of practical relevance for situations occurring in reality. It is the subregion of low values of  $c_0$  and high values of  $T^0$  in this figure. Therefore, a pollutant deposition as a result of the ground water evaporation occurs in this model under quite common natural conditions.

Figure 4 presents elevation lines of the function  $\gamma = \gamma(T^0, c_0)$  in the same rectangle like in Figure 3. For a fixed initial concentration  $c_0$ ,  $\gamma(T^0, c_0)$  increases as a function of  $T^0$ , implying that the velocity of the evaporation front  $V(t) = \gamma(T^0, c_0)\sqrt{D_v}/\sqrt{t}$  computed at fixed  $t$  increases with increasing  $T^0$ . On the other hand, the velocity decreases, for fixed  $T^0$  and increasing  $c_0$ , i.e., higher initial

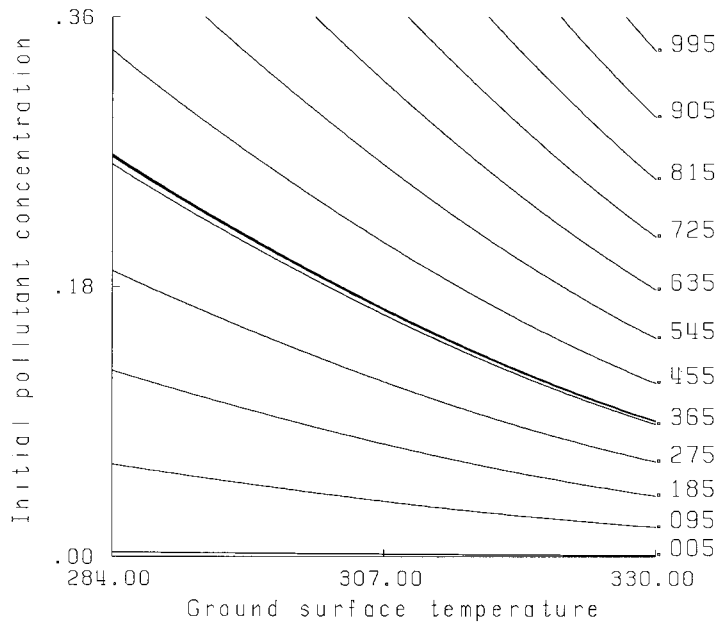


Figure 5. Same as Figure 3 except that  $\nu^0 = 0.002$ .

concentration at the same ground surface temperature renders the propagation of the evaporation front slower. Let  $X_0$  be the initial position of the evaporation front. Then the characteristic diffusion time of vapor is  $T_{v,ch} = X_0^2/D_v$ , and the characteristic diffusion speed of vapor is  $V_{v,ch} = X_0/T_{v,ch} = \sqrt{D_v/T_{v,ch}}$ . From here, the characteristic value of  $\gamma$ , which is its value computed at the characteristic time  $T_{v,ch}$ , is given by  $\gamma(T_{v,ch}) = V(T_{v,ch})/\sqrt{D_v/T_{v,ch}} = V(T_{v,ch})/V_{v,ch}$ . Therefore,  $\gamma(T_{v,ch})$  is the ratio of the front speed computed at the characteristic time  $T_{v,ch}$  to the characteristic diffusion speed of vapor. The characteristic diffusion speed of vapor  $V_{v,ch}$  does not depend on the initial concentration  $c_0$  of vapor. Since the front speed depends strongly on the initial concentration of vapor, so does  $\gamma(T_{v,ch})$ .

Figures 5 and 6 show elevation lines of  $c_+ = c_+(T^0, c_0)$  and of  $\gamma = \gamma(T^0, c_0)$ , respectively, for the case  $\nu^0 = 0.002$  in the same rectangle like in Figure 3. Comparison of Figures 3 and 5 shows that for each fixed pair  $(T^0, c_0)$  considered the concentration on the evaporation front  $c_+(T^0, c_0)$  is greater in the case  $\nu^0 = 0$  than in the case  $\nu^0 = 0.002$ . This result is expected for physical reasons because greater relative humidity of air on the ground surface impedes both the evaporation of water and the diffusion of vapor. Also, the propagation velocity of the evaporation front is greater in the case  $\nu^0 = 0$  than in the case  $\nu^0 = 0.002$ , for each fixed  $(T^0, c_0)$ , see Figures 4 and 6. The elevation line of the elevation level  $c_+(T^0, c_0) = 0.372$  drawn as a thick line in Figure 5 shows that in this case as in the case  $\nu_0 = 0$  there exists a rather large domain of  $(T^0, c_0)$  for which a deposition of the pollutant takes place on the evaporation front. The deposition

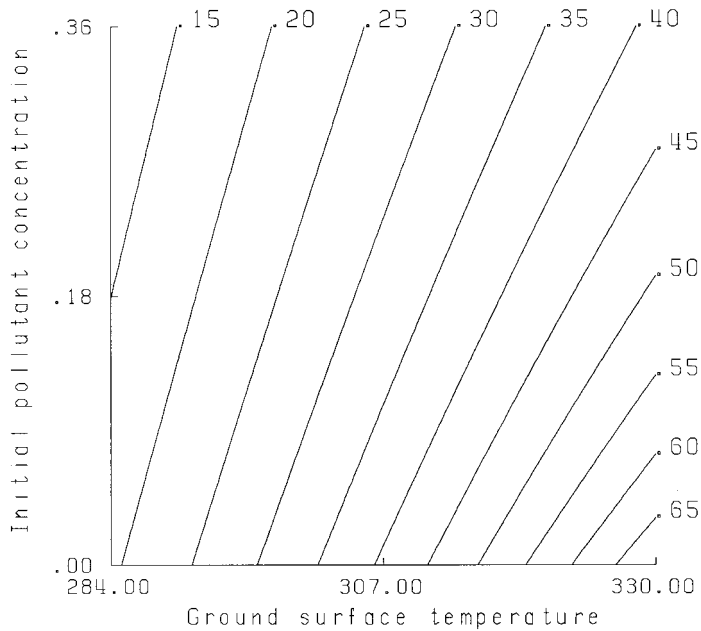


Figure 6. Same as Figure 4 except that  $\nu^0 = 0.002$ .

domain in Figure 5 (case  $\nu^0 = 0.002$ ) is somewhat narrower than that in Figure 3 (case  $\nu^0 = 0$ ).

Figures 7 and 9 present elevation lines of  $c_+ = c_+(T^0, c_0)$  in the rectangle  $(T^0, c_0) \in [308, 330] \times [0, 0.36]$ , for the cases  $\nu^0 = 0.009$  and  $\nu^0 = 0.018$ , respectively. The lower boundary of the temperature range at 308 is the point below which, for some values of  $c_0$  in the range  $[0, 0.36]$ , no solution of the problem exists in the case  $\nu^0 = 0.018$ . The reason for this is as follows. The partial pressure of vapor given by  $P_v = \nu^0 P_a R_v / R_a$  increases as a function of  $\nu^0$ . The solution of the problem exists provided that at each point in the air-vapor domain the partial pressure of vapor is smaller than the pressure of the saturated vapor at the point, i.e.,  $P_v < F(T)$ . An increase of  $\nu^0$  causes an increase of  $P_v$  and a violation of the above inequality for too small values of  $T$ . In Figures 7 and 9 the decrease of  $c_+(T^0, c_0)$  as a function of  $\nu^0$ , for a fixed pair  $(T^0, c_0)$  is more pronounced than in Figures 3 and 5. See, for instance, the location of the elevation lines having the elevation 0.62 in Figures 7 and 9.

In Figures 8 and 10, elevation lines of  $\gamma = \gamma(T^0, c_0)$  are shown in the same rectangle like in Figure 7, for the cases  $\nu^0 = 0.009$  and  $\nu^0 = 0.018$ , respectively. The decrease of the propagation velocity of the evaporation front, when  $\nu^0$  increases from 0.009 to 0.018, is clearly seen in these figures. Also, as in Figures 4 and 6, the gradient of  $\gamma(T^0, c_0)$  in the  $(T^0, c_0)$ -coordinates in Figures 8 and 10 is roughly in the direction of the vector  $(1, -1)$  implying a higher front propagation velocity for greater  $T^0$  and smaller  $c_0$ .

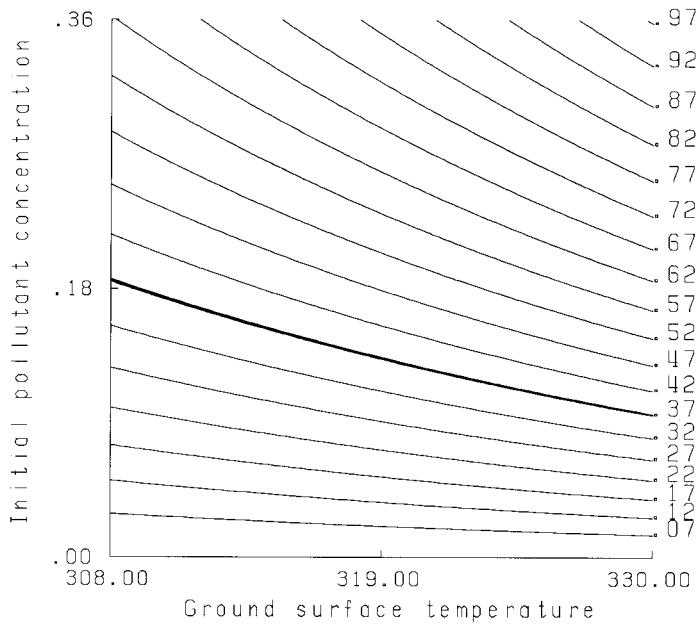


Figure 7. Same as Figure 3 except that  $\nu^0 = 0.009$ .

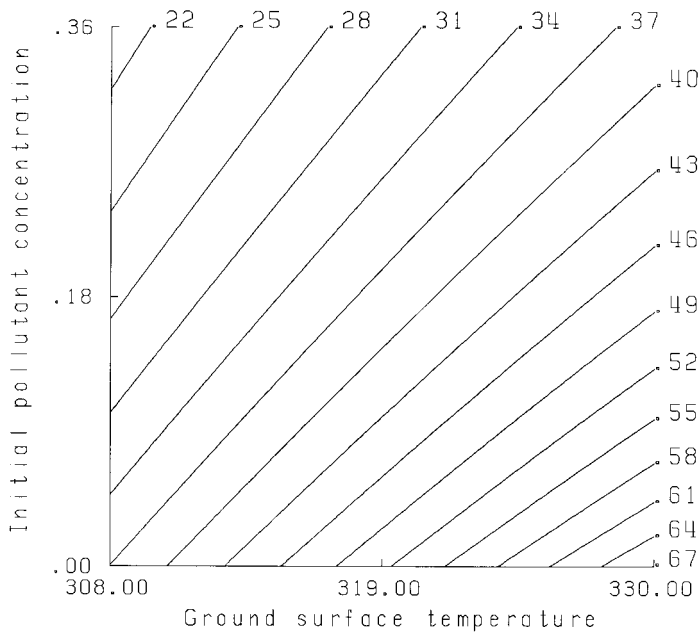


Figure 8. Same as Figure 4 except that  $\nu^0 = 0.009$ .

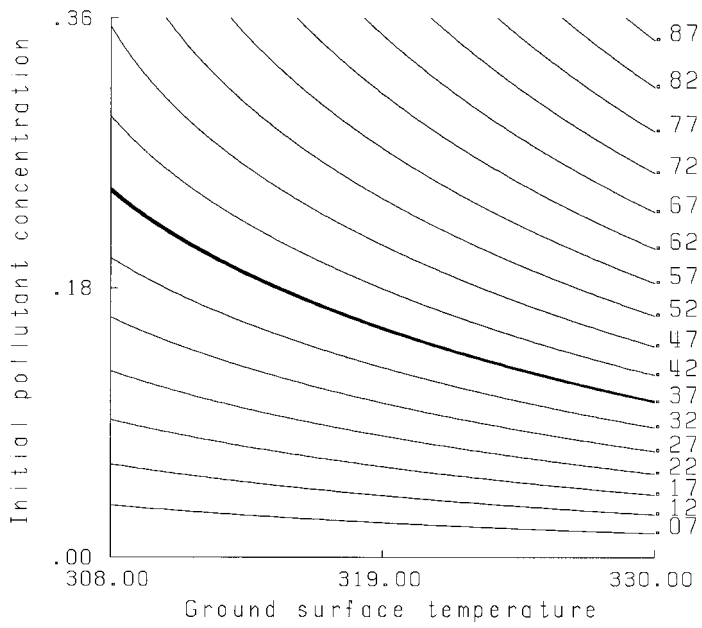


Figure 9. Same as Figure 3 except that  $\nu^0 = 0.018$ .

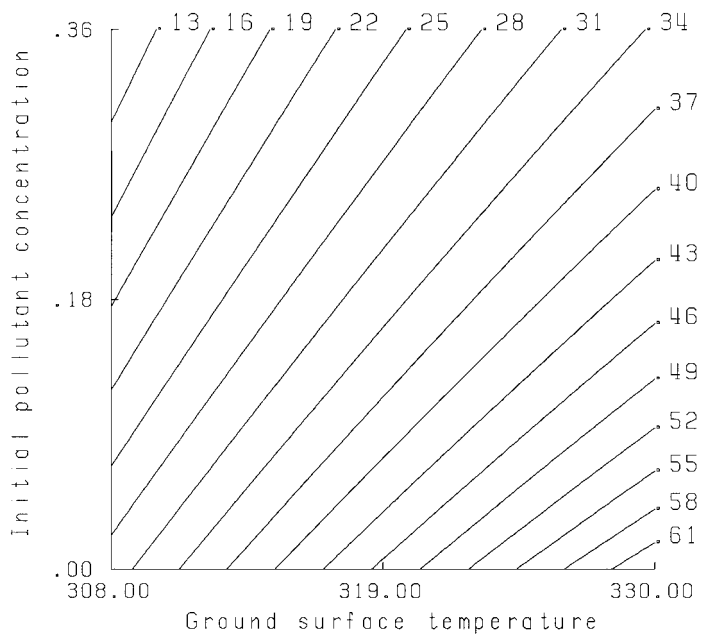


Figure 10. Same as Figure 4 except that  $\nu^0 = 0.018$ .

In each of Figures 7 and 9 the elevation line of the elevation level 0.372 which is higher than the solubility level, for all  $T^0$  considered, is drawn as a thick line. The location of this line in both figures shows that, similar to the cases presented in Figures 3 and 5, increasing  $\nu^0$  renders the deposition domain of  $(T^0, c_0)$  narrower. However, even in the moderately moist and very moist cases shown in Figures 7 and 9, respectively, the deposition domain remains fairly large. In each of these cases this domain contains a realistic subregion relevant for practical purposes which lies in its lower right hand part.

## 5. Conclusions

In this paper, we have proposed a phenomenological mathematical model of the ground water evaporation in the one-dimensional case in the presence of a polluting substance, and investigated its solutions analytically and numerically. The basic interest in developing the model is to study the influence of the evaporation on the vertical concentration distribution of a polluting material dissolved in water. The model accounts for a strong nonlinear coupling that exists between the water domain and the air–vapor domain within a porous soil on the moving evaporation boundary separating between the two domains. Within each domain, the process triggered by the water evaporation in the motionless case is that of a linear diffusion of the relevant physical quantities. For all cases studied, it is shown that the evaporation produces a gradient of the solute concentration within the water domain which is directed upward. Moreover, for NaCl aqueous solutions, for a practically relevant range of the ground surface temperatures and of the initial values of the solute concentration that are below the solubility value, the maximum of the solute concentration that reached on the evaporation front lies beyond the solubility, i.e., it is greater than the critical concentration value starting at which a deposition of the pollutant sets in.

This result emphasizes the environmental significance of the ground water evaporation in the case of polluted water. Furthermore, in the framework of the proposed model, the analysis gives a quantitative estimate for the domain of the basic parameter values, viz. the initial solute concentration and the ground surface temperature, for which pollution of the soil caused by a deposition of the polluting material occurs as a result of the evaporation. Such an estimate can be readily obtained within the present model for any admixture for which the solubility as a function of temperature is given. Hence, we suggest that the proposed model can serve as a tool for estimating the impact of a ground water contamination on the lasting soil pollution that can be caused by the water evaporation under natural conditions.

The analysis of the paper can be extended to the case of a water layer of finite depth. A more difficult yet interesting extension would be to consider the evaporation in the presence of capillary forces. The capillary effect plays a significant role in the process of drying of a porous medium (Whitaker, 1977). An extension of the

proposed mathematical model of the ground water evaporation that accounts for the capillary effect is left as a future task.

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### Appendix

We use the closed analytical form of (37) and of the second of (41) for analyzing the spatial distribution of the solute concentration. Let  $\gamma_0 > 0$  be a solution of (43) for some combination of the parameters. We introduce the notation

$$y = \gamma_0 \sqrt{\frac{D_v}{D_c}}. \quad (44)$$

Then the second of (41) can be expressed as

$$c_+(\gamma_0) = \frac{c_0 e^{-y^2}}{e^{-y^2} - \sqrt{\pi} y \operatorname{erfc}(y)}. \quad (45)$$

Let

$$f(y) = e^{-y^2} - \sqrt{\pi} y \operatorname{erfc}(y). \quad (46)$$

We have

$$\lim_{y \rightarrow \infty} f(y) = -\sqrt{\pi} \lim_{y \rightarrow \infty} \frac{1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy}{1/y} \quad (47)$$

$$= -2 \lim_{y \rightarrow \infty} y^2 e^{-y^2} = 0. \quad (48)$$

The function  $f(y)$  decays monotonously for real  $y$ , since

$$\frac{df(y)}{dy} = 2 \int_0^y e^{-y^2} dy - \sqrt{\pi} < 0, \quad \text{for } y \in \mathbb{R}. \quad (49)$$

Because of  $f(\infty) = 0$ , this implies that  $f(y) > 0$  for all  $y \geq 0$ . Since  $f(y) < e^{-y^2}$ , for  $y > 0$ , from (45) it follows that

$$c_+(\gamma_0) > c_0. \quad (50)$$

The inequality  $c_+(\gamma_0) - c_0 > 0$  and the monotonous decay of the function  $\operatorname{erfc}(z)$ , for  $z > 0$ , imply that the concentration  $c$  given by (37) decays monotonously as a function of  $\xi$ , for positive  $\xi$ , and, hence, it decays monotonously as a function of  $x$ , for  $x > 0$ , for every fixed  $t$ . Since  $\operatorname{erfc}(0) = 1$  and  $\operatorname{erfc}(\infty) = 0$ , we have, for each fixed  $t$ ,

$$c_+ = \max_{x \geq X(t)} c = c|_{x=X(t)+} \quad \text{and} \quad c_0 = \inf_{x \geq X(t)} c = c|_{x=\infty}.$$

Therefore, the process of evaporation produces a vertical redistribution of the initial solute concentration in the ground water domain. At every fixed instant  $t$ , the concentration has a form of a monotonously decreasing function of  $x$  attaining its maximum  $c_+$  on the evaporation front.

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