A 1D numerical study of the salt diffusion in a solar pond using finite difference techniques

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September 6, 2002

Abstract

A simple one dimensional (1D) model for the study of the salt diffusion processes in a solar pond is presented together with the implementation in a computer program using standard finite differences techniques. The convective motions are not explicitly taken into account in this model and comments on their importance are presented. Albeit its simplicity the approach here reported can shed light on the basic effects taking place in the dynamics of a solar pond. The importance of the temperature profile and of the Soret effect is discussed.

1 Introduction

In this study we have considered some aspects of the dynamical behavior of a solar pond. Different physical effects are studied for a one-dimensional model system which can be considered as a column of the actual solar pond along the vertical z axis. The heat and mass exchanges between the column and the rest of the solar pond are neglected and only the exchanges within the column are considered. The convective motion is not taken into account explicitly: this approximation could be considered quite drastic, and we shall comment this aspect latter in the paper. The diffusion equation is solved using numerical procedures based on standard finite difference techniques.

This approach is much simpler than the approaches used in commercial fluid dynamics code, and from a formal point of view it could not be considered fully satisfactory. However a simple one dimensional model allows the possibility of easily interfering with the FORTRAN code, thus possibly adding new effects and test various hypothesis. In this way one can reach a clear comprehension of the basic effects which are relevant for the solar pond dynamics. This comprehension would be more difficult if sophisticated 2D or 3D codes are used.

2 How a solar pond works

Most people know that fluids such as water and air rise when heated. Solar ponds stop this process when large quantities of salt are dissolved in the hot bottom layer of the pond, making it too dense to rise to the surface and cool.

Solar ponds consists of three main layers (see Fig.r̃efsolarpond). The top layer (upper concective zone, UCZ) is cold and has little salt content. The bottom layer (lower convective zone, LCZ) is hot, 70-100i^{o}C and very salty. Separating these two layers is the important gradient zone (non-convective zone, NCZ). Here salt content increases with depth. Water in the gradient can't rise because the water above it has less salt content and is therefore lighter. Similarly, water can't fall because the water below it has a higher salt content and is heavier. Thus the stable gradient zone can act as a transparent insulator, permitting sunlight to be trapped in the hot bottom layer, from which useful heat is withdrawn.

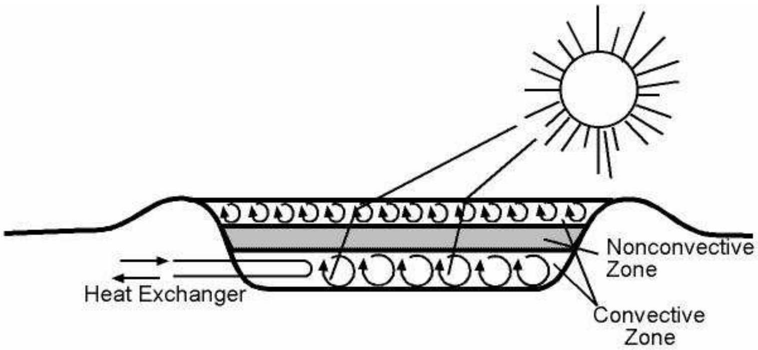

Figure 1: Schematic descriptione of a solar pond

In this simplified description, no attempt is made to describe the hydrodynamic phenomena which influence zone and interface stability, salt and heat transport, and other complex behavior.

3 The diffusion problem

The 1D diffusion problem is

$$\frac{\partial c(z,t)}{\partial t} = -\frac{\partial J}{\partial z} = \frac{\partial}{\partial z}\left(D(z)\frac{\partial c(z,t)}{\partial z}\right) \tag{1}$$

where J is the mass flux, $c(z,t)$ is the concentration of the diffusing solute (function of the position z and of time t) and $D(z)$ is the diffusion coefficient which has been assumed here to be dependent form the position z.

In the following we report the approach presented in ref [1] for the numerical resolution of equation 1. In this scheme we want to find the value of $c(z,t)$ on a regular grid of points in z ($\{z_1, z_2, \cdots, z_{n_z}\}$, $z_{i+1} - z_i = \Delta z$) and t ($\{t_1, t_2, \cdots, t_{n_t}\}$, $t_{i+1} - t_i = \Delta t$). For the sake of simplicity we use the compact formalism $c_{i,j}$ for $c(z_i, t_j)$.

Let us suppose first that $D(z) = cost$. In this case the diffusion equation 1 reduces to

$$\frac{\partial c(z,t)}{\partial t} = D\frac{\partial^2 c(z,t)}{\partial z^2} \tag{2}$$

and the second derivative with respect of z is evaluated using the normal central difference scheme

$$\left.\frac{\partial^2 c(z,t)}{\partial z^2}\right|_{z=z_i,t=t_j} \simeq \frac{c_{i+1,j} + c_{i-1,j} - 2c_{i,j}}{(\Delta z)^2} \tag{3}$$

The resolution of the diffusion equation is therefore performed solving a set of liner equations which can be derived from the equation

$$\frac{c_{i,j} - c_{i,j-1}}{\Delta t} = D\frac{c_{i+1,j} + c_{i-1,j} - 2c_{i,j}}{(\Delta z)^2} \tag{4}$$

This scheme is only *first–order* accurate in time and a best approximation can be obtained using the Crank-Nicholson scheme which is *second–order* accurate in time. In this approach, the second derivative in equation 2 is approximated by the average of its evaluation using equation 3 at time t_j and at time t_{j-1}

$$\frac{c_{i,j} - c_{i,j-1}}{\Delta t} = D\frac{(c_{i+1,j} + c_{i-1,j} - 2c_{i,j}) + (c_{i+1,j-1} + c_{i-1,j-1} - 2c_{i,j-1})}{2(\Delta z)^2} \tag{5}$$

This equation leads to the system of linear equation

$$-\alpha c_{i+1,j} + (1+2\alpha)\, c_{i,j} - \alpha c_{i-,j} = B_{i,j} \tag{6}$$

where

$$\alpha = \frac{D\Delta t}{2(\Delta z)^2} \tag{7}$$

and

$$B_{i,j} = \alpha\,(c_{i+1,j-1} + c_{i-1,j-1} - 2c_{i,j-1}) + c_{i,j-1} \tag{8}$$

Let us now consider the case of a diffusion coefficient which is function of z. We shall discuss at the end of this section the origin of such a dependence: we suppose here to know the value of D on the n_z values of z_i. The same strategy outlined above can be applied to equation 1 and, if everything is appropriately centered[1], one gets

$$\frac{c_{i,j} - c_{i,j-1}}{\Delta t} = \frac{D_{i+\frac{1}{2}}\,(c_{i+1,j} - c_{i,j}) - D_{i-\frac{1}{2}}\,(c_{i-1,j} - c_{i,j})}{(\Delta z)^2} \tag{9}$$

where

$$D_{i+\frac{1}{2}} = \frac{D(z_{i+1}) + D(z_i)}{2} \tag{10}$$

$$D_{i-\frac{1}{2}} = \frac{D(z_{i-1}) + D(z_i)}{2} \tag{11}$$

The *second–order* accurate in time Crank-Nicholson generalization of equation 9 can be easily obtained

$$\frac{c_{i,j} - c_{i,j-1}}{\Delta t} = \frac{D_{i+\frac{1}{2}}\left[(c_{i+1,j} - c_{i,j}) + (c_{i+1,j-1} - c_{i,j-1})\right] - D_{i-\frac{1}{2}}\left[(c_{i-1,j} - c_{i,j}) + (c_{i-1,j-1} - c_{i,j-1})\right]}{2\left(\Delta z\right)^2} \tag{12}$$

Equation 12 can be rewritten in the form of a system of linear equations (one set for each time t_j)

$$-\alpha_{i+\frac{1}{2}} c_{i+1,j} + \left(1 + \alpha_{i+\frac{1}{2}} + \alpha_{i-\frac{1}{2}}\right) c_{i,j} - \alpha_{i-\frac{1}{2}} c_{i-1,j} = B_{i,j} \tag{13}$$

where

$$\alpha_{i+\frac{1}{2}} = \frac{D_{i+\frac{1}{2}} \Delta t}{2\left(\Delta z\right)^2} \tag{14}$$

$$\alpha_{i-\frac{1}{2}} = \frac{D_{i-\frac{1}{2}} \Delta t}{2\left(\Delta z\right)^2} \tag{15}$$

and

$$B_{i,j} = \alpha_{i+\frac{1}{2}}\left(c_{i+1,j-1} - c_{i,j-1}\right) - \alpha_{i-\frac{1}{2}}\left(c_{i-1,j-1} - c_{i,j-1}\right) + c_{i,j-1} \tag{16}$$

The systems of linear equations 13 can be written in matrix form

$$\mathbf{A}\mathbf{C}_j = \mathbf{B}_j \qquad \forall j = 2, n_t \tag{17}$$

and it can be easily solved by standard mathematical libraries such as for instance the LAPACK ones[2] with the following initial and boundary conditions, which complete the system of linear equation 17:

- initial condition: define $c(z, 0)$;
- boundary conditions at each time t_j: define $c_{1,j}$ and $c_{n_z,j}$.

We note that the matrix $\mathbf{A}$ is a symmetric tridiagonal matrix and does not depend on the time index j.

The boundary conditions can be set on the basis of two physical hypothesis on the border of our system:

1. The border is impermeable (for instance as in the case of a physical wall). The flux across the border must be zero and therefore

$$J = -D\frac{\partial c(z,t)}{\partial z} \simeq -D\frac{c_{i+1,j} - c_{i,j}}{\Delta z} = 0 \tag{18}$$

$$\downarrow$$

$$c_{i+1,j} = c_{i,j} \tag{19}$$

If this condition is imposed for instance at $z = 0$, we have $c_{2,j} = c_{1,j}$ and the $i = 2$ case in equation 13 is consequently modified as

$$-\alpha_{2+\frac{1}{2}} c_{3,j} + \left(1 + \alpha_{2+\frac{1}{2}}\right) c_{2,j} = B_{2,j} \tag{20}$$

Analogously for $z = z_{\max}$ we have $c_{n_z,j} = c_{n_z-1,j}$ and the $i = n_z - 1$ case in equation 13 is

$$-\alpha_{n_z-1-\frac{1}{2}} c_{n_z-2,j} + \left(1 + 2\alpha_{n_z-1-\frac{1}{2}}\right) c_{n_z-1,j} = B_{n_z-1,j} \tag{21}$$

2. The border is an infinite reservoir which is able to maintain constant in time the concentration on it thus releasing/adsorbing any mass flux to/from the system. In this case the boundary condition (for instance at $z = 0$) can be set as

$$c_{1,j} = c_{1,j-1} \tag{22}$$

and the $i = 2$ case in equation 13 is

$$-\alpha_{2+\frac{1}{2}} c_{3,j} + \left(1 + \alpha_{2+\frac{1}{2}} + \alpha_{2-\frac{1}{2}}\right) c_{2,j} = B_{2,j} + \alpha_{2-\frac{1}{2}} c_{1,j-1} \tag{23}$$

An analogous condition can be written for $z = z_{\max}$.

The scheme outlined above has been implemented in a FORTRAN 77 computer code (called DIFFIN): the sets of linear equations 17 are solved using the DGTSV subroutine of LAPACK mathematical library and the boundary conditions 1 and 2 can be separately set on $z = 0$ and $z = z_{\max}$.

Once the diffusion problem has been solved, thus obtaining the value for $c_{i,j}$, the program compute the following properties:

- The flux, $J_{i,j}$ (in $\frac{\text{kg}}{\text{m}^2 \cdot day}$), at any point z_i, t_j using the approximation which is correct to second order

$$\begin{aligned} J_{i,j} &= -D_i \left. \frac{\partial c(z,t)}{\partial z} \right|_{z=z_i, t=t_j} \\ &\simeq -D_i \frac{c_{i+1,j} - c_{i-1,j}}{2\Delta z} \end{aligned} \tag{24}$$

For the first and the last point the flux is

$$J_{1,j} = -D_1 \frac{c_{2,j} - c_{1,j}}{\Delta z} \qquad J_{n_z,j} = -D_{n_z} \frac{c_{n_z,j} - c_{n_z-1,j}}{\Delta z} \tag{25}$$

which is only correct to the first order.

- The density, $\rho_{i,j}$ (in $\frac{\text{kg}}{\text{m}^3}$), at any point z_i, t_j: it is a function of the temperature T and of the salinity S (in g/kg). In the case of a solution of NaCl in water ρ is given by [3]:

$$\rho(z,t) = 1000 \times \left\{ 1 - \frac{T+a}{b \times (T+c)} \times (T-d)^2 \right\} + e(T) \times S + f(T) \times S^{\frac{3}{2}} + g \times S^2 \tag{26}$$

where

$$\begin{aligned} e(T) &= 8.24493 \cdot 10^{-1} - 4.0899 \cdot 10^{-3} \times T + 7.6438 \cdot 10^{-5} \times T^2 + \\ &\quad -8.2467 \cdot 10^{-7} \times T^3 + 5.3675 \cdot 10^{-9} \times T^4 \end{aligned} \tag{27}$$

$$f(T) = -5.724 \cdot 10^{-3} + 1.0227 \cdot 10^{-4} \times T - 1.6546 \cdot 10^{-6} \times T^2 \tag{28}$$

$$g = 4.8314 \cdot 10^{-4} \tag{29}$$

We do not have direct access to the salinity because it is, in its turn, a function of the concentration and of the density

$$S(z,t) = \frac{c(z,t)}{\rho(z,t)} \tag{30}$$

Therefore the calculation of $\rho_{i,j}$ has been implemented in an iterative scheme: we consider first $S_{i,j} = c_{i,j}$, then compute $\rho_{i,j}$ using equation 26 and finally compute $S_{i,j}$ using equation 30. The process is repeated until the variation of c between two successive steps is lower than a certain threshold. The salinity function $S(z,t)$ is therefore another output property of the program.

4 Solar pond dependent terms

In order to completely define the strategy that we have implemented, a consideration must be done on the dependence of the diffusion coefficient D and of the temperature T on the height z. While the derivation outlined in section 3 is completely general for any diffusion problem, the form of these terms are specific of the solar pond system and they are treated in this section.

For D we consider here the equation [4, 5]

$$D_i = D_0 \times [1 + 0.029\,(T_i - 20)] \tag{31}$$

which gives the dependence of D on the temperature (in °C) for a solution of NaCl in water. D_0 is equal to $1.39 \cdot 10^{-9}$ in m^2/s or $1.20096 \cdot 10^{-4}$ in m^2/day. We have supposed that the temperature profile (which will be defined in the following) is constant in time and depends only the space index i.

A more precise equation, in which also the dependence on the salinity is considered, is obtained by a least square fit to the International Critical Tables for a range of temperature between 5 and 100 °C and for a salinity range between 0 and 20% is [6]

$$D_{i,j} = \left(8.16 + 0.255T_i + 0.00254T_i^2 - 0.28S_{i,j} + 0.0147S_{i,j}^2\right) \times 10^{-10} \tag{32}$$

where S is the salinity in weight percent ($S = c/\rho \times 100$) and $D_{i,j}$ is in m^2/s. It is clear that equation 32 for D makes the study of mass diffusion a complex non linear problem. We have implemented two alternative solutions in order to keep the approach linear and simple:

1. $D_{i,j}$ is computed using the salinity $S_{i,j-1}$ at time t_{j-1}, which is a very good approximation, given that D has a small dependence on S and that S (or c) changes very slowly from one time step to the next one;
2. for each time step t_j the concentration c is computed iteratively, each step consisting in the computation of D using the values of S obtained at the previous step and recomputing c. For the first step the values of D are obtained following approximation 1. The iterative approach is stopped when a convergence criterion is satisfied.

Finally the dependence of the temperature on the height z can be obtained by successive integrations of the heat conduction equation[7]:

$$-k\frac{d^2T}{dz^2} = \dot{q}, \tag{33}$$

where k is the thermal conductivity, $\dot{q}$ is the heat absorbed per unit of volume and time and can be expressed in terms of the gradient of the solar power density:

$$\dot{q} = -\frac{dW}{dz} = -\frac{W_0[a - b\log(x)]}{dz} = -\frac{d}{dz}\left\{W_0\left[a - b\ln\left(\frac{z}{cos\theta_r}\right)\right]\right\} = \frac{W_0 b}{z} \tag{34}$$

with a=0.4415 and b = 0.094085 empirical parameters, and θ_r the refraction angle.

The final expressions for the temperature gradient and temperature profile are given by:

$$\frac{\partial T}{\partial z} = -\frac{W_0 b}{k}\ln(z) + C_1 \tag{35}$$

$$T(z) = -\frac{W_0 b}{k}\left[z\ln(z) - z\right] + C_1 z + C_2 \tag{36}$$

where W_0 is the solar power density (in $\mathrm{Watt}/\left(\mathrm{m}^2 \cdot \mathrm{s}\right)$), k is the thermal conductivity (in $\mathrm{Watt}/\left(\mathrm{m} \cdot \mathrm{K}\right)$), b is an empirical factor, T_l and T_u are the temperature of the LCZ and UCZ, respectively and the two constants C_1 and C_2 are given by

$$C_1 = \frac{T_l - T_u}{z_l - z_u} - \frac{W_0 b}{k}\left[1 - \frac{z_u\ln(z_u) - z_l\ln(z_l)}{z_u - z_l}\right] \tag{37}$$

$$C_2 = T_l + \frac{W_0 b}{k}\left[z_l\ln(z_l) - z_l\right] - C_1 z_l \tag{38}$$

5 The convection within the solar pond

A complete description of convective motions needs an approach more complex than the one described in section 3. Moreover, given that the convective motions develop on a time scale much shorter than diffusion, the inclusion of convection needs a smaller time step in the numerical procedure thus strongly increasing the total CPU time of the simulation. On the basis on this consideration we have therefore decided to avoid an explicit treatment of convection. On the other hand some considerations about the convective motions, are needed to make our approach more realistic.

Let us first consider the intermediate salt-gradient zone. This zone plays a central role in the solar pond efficiency because it is designed in order to prevent the convective motions which would mix the high temperature lower layers with the low temperature superficial layers, thus improving the energy dispersion to the atmosphere. Simple considerations suggest that the convective motions are hindered once the density gradient is negative (the density is a decreasing function of the height z). This is allowed only in the presence of a sufficiently negative concentration gradient given that the density is an increasing/decreasing function of the concentration/temperature. Therefore in the following we shall not consider convective motions in the NCZ, although taking care to verify that the density profile is such that these motions are hindered.

Actually the requirement of a negative density gradient is a necessary but not sufficient condition: a deeper analysis (Rayleigh analysis) [4] shows that the concentration gradient needed for maintaining the stability must satisfy the following inequality:

$$\frac{\partial c}{\partial z} + \frac{(\nu + K_T)\left(\frac{\partial \rho}{\partial T}\right)\left(\frac{\partial T}{\partial z}\right)}{(\nu + D)\left(\frac{\partial \rho}{\partial c}\right)} \leq 0 \tag{39}$$

where ν is the kinematic viscosity (in m^2/s), K_T is the thermal diffusivity (in m^2/s). The derivatives $\frac{\partial \rho}{\partial T}$ and $\frac{\partial \rho}{\partial c}$ ($= \frac{1}{\rho}\frac{\partial \rho}{\partial S}$) are obtained from equation 26, while $\frac{\partial T}{\partial z}$ is given by equation 35. Let us note that with respect to reference [4] the direction of the inequality is inverted due to the different definition of z.

In the LCZ and UCZ, as their name indicate, the convective motions are allowed and play a relevant role. However, as already said, convective motions develops on a time scale much shorter than the diffusive motions, and therefore we can suppose that the convective motions maintain the LCZ and UCZ temperature and concentration homogeneous at any time step.

We have implemented the possibility of averaging the concentration in the LCZ and UCZ, after the solution of the diffusion equation at any time step. This procedure is controlled by a keyword in the input file. We consider the LCZ and UCZ temperatures always homogeneous.

6 The thermodiffusion (Soret effect)

A term which is very important to study in the case of the solar pond dynamics is the Soret effect. It is due to the action of a temperature gradient on the mean motion of a particle. A detailed study on the origin of such an effect is quite complex and we have used the empirical formulation reported by Sherman [8], where the diffusive flux in equation 2 is modified adding a term due to the temperature gradient

$$J = J_D + J_S = -D\frac{\partial c}{\partial z} - D\ s\ c\ \frac{m_2}{m_1 + m_2}\frac{\partial T}{\partial z} \tag{40}$$

where J_D is the flux due to the usual diffusion process, J_S is the flux due to the Soret effect, s is the Soret coefficient (in 1/K), m_1 is the molar concentration of the salt and m_2 is the molar concentration of the water. We assume that the Soret coefficient is in general a function of z. The ratio involving m_1 and m_2 can be written as

$$\frac{m_2}{m_1 + m_2} = \left(1 + \frac{MW_2}{MW_1}\frac{c}{\rho - c}\right)^{-1} \tag{41}$$

where MW_1 and MW_2 are the molar weight of the salt and of the water, respectively. Therefore the concentration variation due to the Soret effect is

$$\frac{\partial c(z,t)}{\partial t} = -\frac{\partial J_S}{\partial z} = \frac{\partial}{\partial z}\left(f(z,t)\frac{\partial T}{\partial z}\right) \tag{42}$$

where

$$f(z,t) = \frac{D(z)s(z)c(z,t)}{1 + \frac{MW_2}{MW_1}\frac{c(z,t)}{\rho(z,t) - c(z,t)}} \tag{43}$$

Equation 42 can be solved using the technique presented in section 3, and we get

$$\frac{c_{i,j} - c_{i,j-1}}{\Delta t} = \frac{f_{i+\frac{1}{2},j}\left(T_{i+1} - T_i\right) - f_{i-\frac{1}{2},j}\left(T_i - T_{i-1}\right)}{\left(\Delta z\right)^2} \tag{44}$$

for the first order approximated in time method and

$$\frac{c_{i,j} - c_{i,j-1}}{\Delta t} = \frac{\left[f_{i+\frac{1}{2},j} + f_{i+\frac{1}{2},j-1}\right]\left(T_{i+1} - T_i\right) - \left[f_{i-\frac{1}{2},j} + f_{i-\frac{1}{2},j-1}\right]\left(T_i - T_{i-1}\right)}{2\left(\Delta z\right)^2} \tag{45}$$

for the second order approximated in time Crank-Nicholson method.

The function $f(z,t)$ can be written as

$$f(z,t) = g(z,t) \cdot c(z,t) \tag{46}$$

where

$$g(z,t) = \frac{D(z)s(z)}{1 + \frac{MW_2}{MW_1}\frac{c(z,t)}{\rho(z,t)-c(z,t)}} \tag{47}$$

and using the notation $g_{i,j}$ for $g(z_i,t_j)$

$$g_{i,j} = \frac{D_i s_i}{1 + \frac{MW_2}{MW_1}\frac{c_{i,j}}{\rho_{i,j}-c_{i,j}}} \tag{48}$$

We note that $f(z,t)$ is a non linear function of the concentration $c(z,t)$, so equations 44 or 45 are a system of non linear equations which complicate the formulation.

In order to keep the problem tractable with simple methods, we have therefore introduced other approximations.

The simplest approximation is to consider $g_{i,j} = g_{i,j-1}$ which makes equations 44 and 45 again linear. In order to estimate the error introduced with this approximation, let us call $\varepsilon_{i,j}$ the variation of $c/\left(\rho - c\right)$ at z_i passing from t_{j-1} to t_j

$$\frac{c_{i,j}}{\rho_{i,j} - c_{i,j}} = \frac{c_{i,j-1}}{\rho_{i,j-1} - c_{i,j-1}} + \varepsilon_{i,j} \tag{49}$$

which is supposed to be very small with respect to 1 (given that the ratio $c/\left(\rho - c\right)$ is expected to be in the range $[0:0.3]$ and small variations of c are requested in order to have correct results). Using Eq. 49 and the approximation $1/(1+x) \simeq (1-x)$, with $x = \varepsilon_{i,j}\frac{\frac{MW_2}{MW_1}}{1+\frac{MW_2}{MW_1}\frac{c_{i,j-1}}{\rho_{i,j-1}-c_{i,j-1}}}$ we have

$$\begin{aligned}
g_{i,j} &= \frac{D_i s_i}{1 + \frac{MW_2}{MW_1}\frac{c_{i,j}}{\rho_{i,j}-c_{i,j}}} = \frac{D_i s_i}{1 + \frac{MW_2}{MW_1}\frac{c_{i,j-1}}{\rho_{i,j-1}-c_{i,j-1}}} \times \frac{1}{1 + \varepsilon_{i,j}\frac{\frac{MW_2}{MW_1}}{1+\frac{MW_2}{MW_1}\frac{c_{i,j-1}}{\rho_{i,j-1}-c_{i,j-1}}}} \\
&\simeq \frac{D_i s_i}{1 + \frac{MW_2}{MW_1}\frac{c_{i,j-1}}{\rho_{i,j-1}-c_{i,j-1}}} \times \left[1 - \varepsilon_{i,j}\frac{\frac{MW_2}{MW_1}}{1 + \frac{MW_2}{MW_1}\frac{c_{i,j-1}}{\rho_{i,j-1}-c_{i,j-1}}}\right] \\
&\simeq g_{i,j-1}\left[1 - \varepsilon_{i,j}\frac{\frac{MW_2}{MW_1}}{1 + \frac{MW_2}{MW_1}\frac{c_{i,j-1}}{\rho_{i,j-1}-c_{i,j-1}}}\right]
\end{aligned} \tag{50}$$

Noting that $\frac{MW_2}{MW_1}\frac{c_{i,j-1}}{\rho_{i,j-1}-c_{i,j-1}} \geq 0$ and remembering that $\varepsilon_{i,j}$ is supposed to be very small with respect to 1, we can conclude that the replacement of $g_{i,j}$ with $g_{i,j-1}$ can be considered a good approximation.

With the approximation

$$g_{i,j} \simeq g_{i,j-1} = \frac{D_i s_i}{1+\frac{MW_2}{MW_1}\frac{c_{i,j-1}}{\rho_{i,j-1}-c_{i,j-1}}} \tag{51}$$

equations 44 and 45 are linear:

$$\frac{c_{i,j}-c_{i,j-1}}{\Delta t} = \frac{\left(g_{i+1,j-1}c_{i+1,j}+g_{i,j-1}c_{i,j}\right)\left(T_{i+1}-T_i\right)-\left(g_{i,j-1}c_{i,j}+g_{i-1,j-1}c_{i-1,j}\right)\left(T_i-T_{i-1}\right)}{2\left(\Delta z\right)^2} \tag{52}$$

for the first order approximated in time method and

$$\begin{aligned}\frac{c_{i,j}-c_{i,j-1}}{\Delta t} &= \frac{1}{4\left(\Delta z\right)^2}\cdot\left\{\left[g_{i+1,j-1}\left(c_{i+1,j}+c_{i+1,j-1}\right)+g_{i,j-1}\left(c_{i,j}+c_{i,j-1}\right)\right]\left(T_{i+1}-T_i\right)+\right.\\ &\left.-\left[g_{i,j-1}\left(c_{i,j}+c_{i,j-1}\right)+g_{i-1,j-1}\left(c_{i-1,j}+c_{i-1,j-1}\right)\right]\left(T_i-T_{i-1}\right)\right\}\end{aligned} \tag{53}$$

for the Crank-Nicholson method.

The system of linear equations to be solved for the diffusion problem in presence of the Soret term using the Crank-Nicholson method is finally

$$-\beta_{i+\frac{1}{2},j}c_{i+1,j}+\left(1+\gamma_{i,j}\right)c_{i,j}-\beta_{i-\frac{1}{2},j}c_{i-1,j}=B'_{i,j} \tag{54}$$

where

$$\beta_{i+\frac{1}{2},j}=\alpha_{i+\frac{1}{2}}+\frac{g_{i+1,j-1}\left(T_{i+1}-T_i\right)\Delta t}{4\left(\Delta z\right)^2} \tag{55}$$

$$\beta_{i-\frac{1}{2},j}=\alpha_{i-\frac{1}{2}}-\frac{g_{i-1,j-1}\left(T_i-T_{i-1}\right)\Delta t}{4\left(\Delta z\right)^2} \tag{56}$$

$$\gamma_{i,j}=\alpha_{i+\frac{1}{2}}+\alpha_{i-\frac{1}{2}}+\frac{g_{i,j-1}\left(T_{i+1}+T_{i-1}-2T_i\right)\Delta t}{4\left(\Delta z\right)^2} \tag{57}$$

and

$$\begin{aligned}B'_{i,j} &= B_{i,j}+\frac{\left(g_{i+1,j-1}c_{i+1,j-1}+g_{i,j-1}c_{i,j-1}\right)\left(T_{i+1}-T_i\right)\Delta t}{4\left(\Delta z\right)^2}+\\ &-\frac{\left(g_{i,j-1}c_{i,j-1}+g_{i-1,j-1}c_{i-1,j-1}\right)\left(T_i-T_{i-1}\right)\Delta t}{4\left(\Delta z\right)^2}\end{aligned} \tag{58}$$

(the terms $\alpha_{i+\frac{1}{2}}$, $\alpha_{i-\frac{1}{2}}$ and $B_{i,j}$ are defined in section 3).

The system of linear equations 54 can be written in the matrix form

$$\mathbf{A}_j \mathbf{C}_j = \mathbf{B}_j \qquad \forall j = 2, n_t \tag{59}$$

Let us note that with respect to equation 17, with the inclusion of the Soret effect, the matrix **A** is no more symmetric (while remaining tridiagonal) and it is dependent from the time index j.

The numerical scheme is completed defining the boundary conditions.

1) If the requirement of concentration constant in time ($c_{1,j} = c_{1,j-1} = c_{1,1}$ or $c_{n_z,j} = c_{n_z,j-1} = c_{n_z,1}$) is imposed on the border one has

$$-\beta_{2+\frac{1}{2},j} c_{3,j} + (1 + \gamma_{2,j})\, c_{2,j} = B'_{2,j} + \beta_{2-\frac{1}{2},j} c_{1,1} \tag{60}$$

or

$$-\beta_{n_z-1-\frac{1}{2},j} c_{n_z-2,j} + (1 + \gamma_{n_z-1,j} - \beta_{n_z-1})\, c_{n_z-1,j} = B'_{n_z-1,j} + \beta_{n_z-1+\frac{1}{2},j} c_{n_z,1} \tag{61}$$

2) The requirement of zero flux across the border is in this case more complex than in the case of a purely diffusive system. Remembering equation 40, we have

$$-D(z)\frac{\partial c(z,t)}{\partial z} - \frac{D(z)s(z)c(z,t)}{1 + \frac{MW_2}{MW_1}\frac{c(z,t)}{\rho(z,t)-c(z,t)}}\frac{\partial T(z)}{\partial z} = 0 \tag{62}$$

If this condition is imposed at z_1 one gets

$$-D_1 \frac{c_{2,j} - c_{1,j}}{\Delta z} - g_{1,j} c_{1,j} \frac{T_2 - T_1}{\Delta z} = 0 \tag{63}$$

$$c_{1,j} = \left[1 - \frac{g_{1,j}\,(T_2 - T_1)}{D_1}\right]^{-1} c_{2,j} \tag{64}$$

and the second line of the system of linear equation 59 becomes

$$-\beta_{2+\frac{1}{2},j} c_{3,j} + \left(1 - \gamma_{2,j} - \beta_{2-\frac{1}{2},j}\left[1 + \frac{g_{1,j}\,(T_2 - T_1)}{D_1}\right]^{-1}\right) c_{2,j} = B'_{2,j} \tag{65}$$

Analogously if zero flux is imposed at n_z one obtains

$$\left(1+\gamma_{n_z-1,j}-\beta_{n_z-1-\frac{1}{2},j}\left[1+\frac{g_{n_z,j}\left(T_{n_z}-T_{n_z-1}\right)}{D_{n_z-1}}\right]^{-1}\right)c_{n_z-1,j}-\beta_{n_z-1-\frac{1}{2},j}c_{n_z-2,j}=B'_{n_z-1,j} \quad (66)$$

A higher level of approximation is reached by using an iterative approach: the values of $g_{i,j}$ for a given time t_j are first computed as indicated in equation 51. Using these values, equations 52 or 53 are solved thus obtaining $c_{i,j}$ which can be used to recompute $g_{i,j}$. The process is repeated until a convergence criterion is satisfied. The two approaches have been implemented in our code.

7 Discussion of the results

The DIFFIN code is a flexible tool to study the salt diffusion in a solar pond, allowing the management of a large number of parameters, initial and boundary conditions.

The results of a series of simulations are presented in this section to test the validity of the model.

The solar pond was dimensioned with the following thickness: 0.5 m for the UCZ, 1.0 m for the LCZ, and 2.0 m for the NCZ. A solar power density W_0 of 300 W/m^2 at the water surface and a constant thermal conductivity of 0.64 W/m/K were considered.

7.1 The temperature and initial concentration profiles

We have assumed a constant and uniform temperature within the LCZ and UCZ, 25^{o}C and 90^{o}C, respectively. The temperature profile, computed using equation 36, is plotted in Fig. 2-left.

Th initial condition of the system is defined by an assigned NaCl concentration profile (expressed

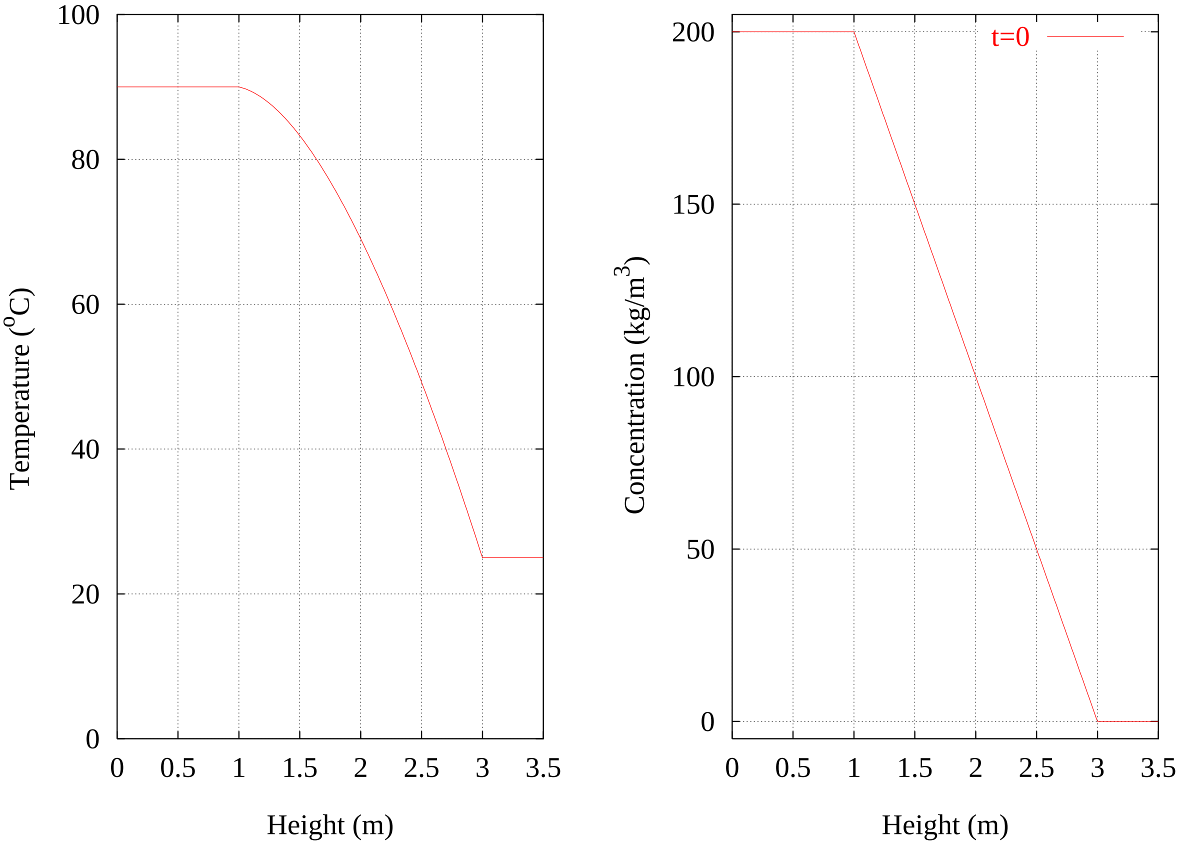

Figure 2: Left: solar pond temperature (^{o}C). Right: initial concentration (kg/m^3)

in kg/m^3). Such profile is a linear decreasing function of the height within the NCZ layer, and it has constant values within the LCZ and UCZ. We have assumed C_{LCZ}=200 kg/m^3, and C_{UCZ}=0 kg/m^3, and the initial condition is plotted in Fig. 2-right.

7.2 The boundary condition

The DIFFIN code can consider two kinds of boundary conditions; that is, zero flux or constant concentration. The first kind of condition means that the system is closed $(J(z = 0 \text{ m}) = 0$

and $J(z = 3.5\ \text{m}) = 0$) and, therefore, the salt mass must be conserved within the system. We recall that the flux J is given by the sum of the diffusion and thermodiffusion contributions: for the Soret coefficient (see equation 40, we have used s(z)=s=2.25x10^{-3} K^{-1} (an approximated constant value obtained by averaging limiting values given in literature [8]).

The second kind of condition means that a continuous addition/extraction of salt is done in the LCZ/UCZ , in order to maintain constant concentration at the boundaries.

7.3 The steady state

The steady state is reached when the flux, J, becomes constant everywhere in the system.

Of course, if the system is closed, the steady state condition implies zero flux everywhere. In this case, if thermodiffusion is neglected, the zero flux condition leads to constant concentration (even with $D = D(T)$). On the other hand, if the thermodiffusion is taken into account, at the steady state the system still has a concentration gradient (Soret effect). This behavior is shown in Fig. 3 where we have compared the steady state with and without the thermodiffusion contribution. Anyway, the salt diffusion is a very slow process: under this conditions, the concentration profile does not show any sensible change after about 60 years with the zero flux boundary condition.

The mass was conserved over the time, with a relative variation of the order of 0.06%, which could be further reduced by increasing the number of grid points (here, we have considered a space and time discretization with Δz=0.01 m and Δt=2.8 d).

7.4 The transient

A series of test cases have been considered to study the temporal evolution of the salt concentration in a solar pond.

In a first simulation we have assumed a zero flux boundary condition at z=0 and z=3.5 m. More-

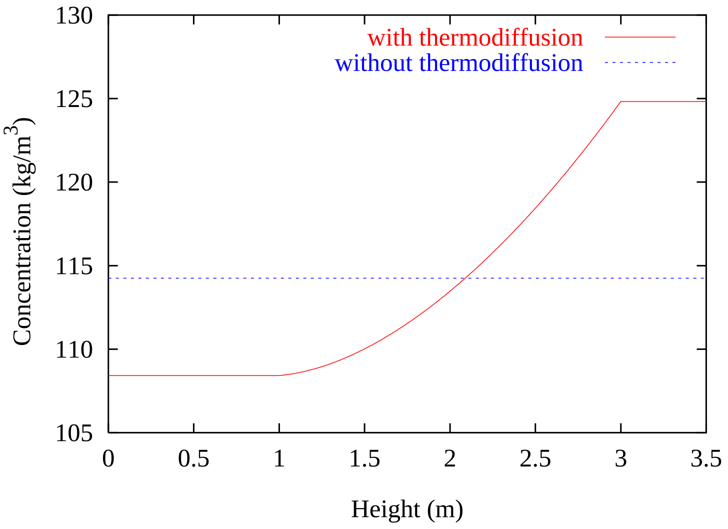

Figure 3: Comparison of steady state concentration profiles with and without thermodiffusion. Concentrations are in kg/m^3.

over, after each time step, due to the decrease/increase of salt concentration in the LCZ/UCZ (because of the salt diffusion), and due to the convective motion within these two layers, an averaging of the salt concentration is done, in order to maintain the concentration uniform within the LCZ and UCZ. Moreover, thermodiffusion has been taken into account. The results of the simulation of 10 years of salt diffusion in the solar pond are plotted in Fig. 4.

A particular care must be taken in the control of the salt gradient stability within the NCZ. This is done by calculating the stability function, which results from the Rayleigh analysis (see Eq. 39), and verifying that its value is always lower than zero everywhere in the NCZ. In Fig. 5 the stability condition is plotted for a transient of 14 years, showing that, during the first 10 years the density gradient is able to suppress the convection within the NCZ.

The effect of the thermodiffusion is to decrease the stability of the salt-gradient in the NCZ. In fact, if the thermodiffusion is neglected, the system becomes instable slower, as shown in Fig 6, where the results of the simulation of a transient of 12 years are compared in the cases when the Soret effect is considered or neglected.

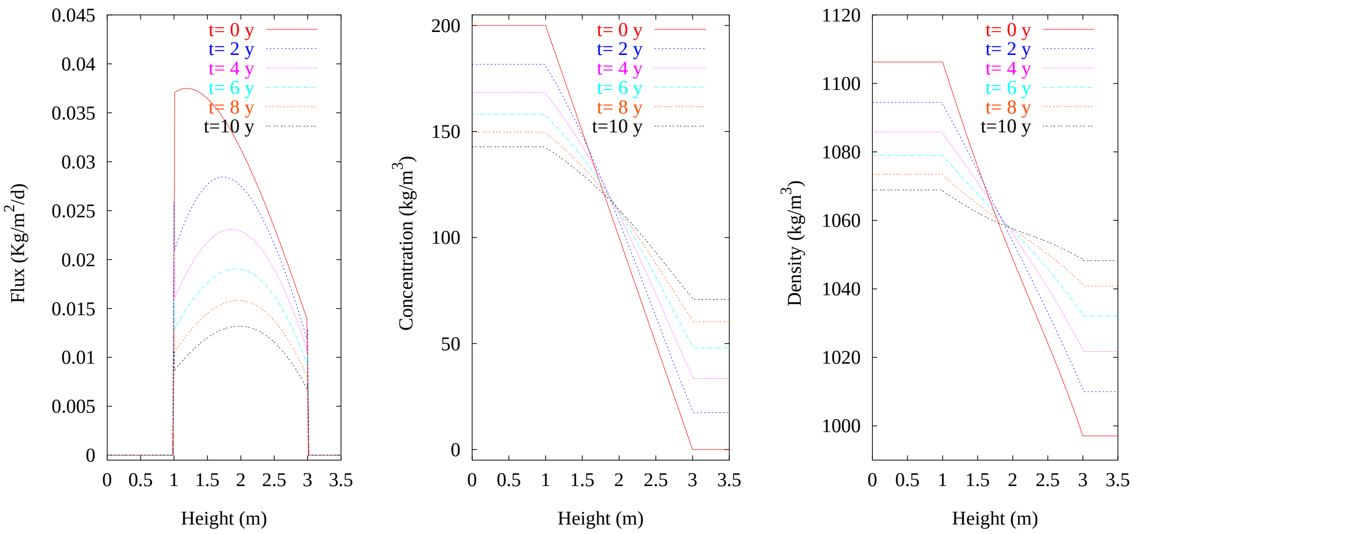

Figure 4: Transient (10 years) behavior of the flux (left), concentration (center), and density (right)

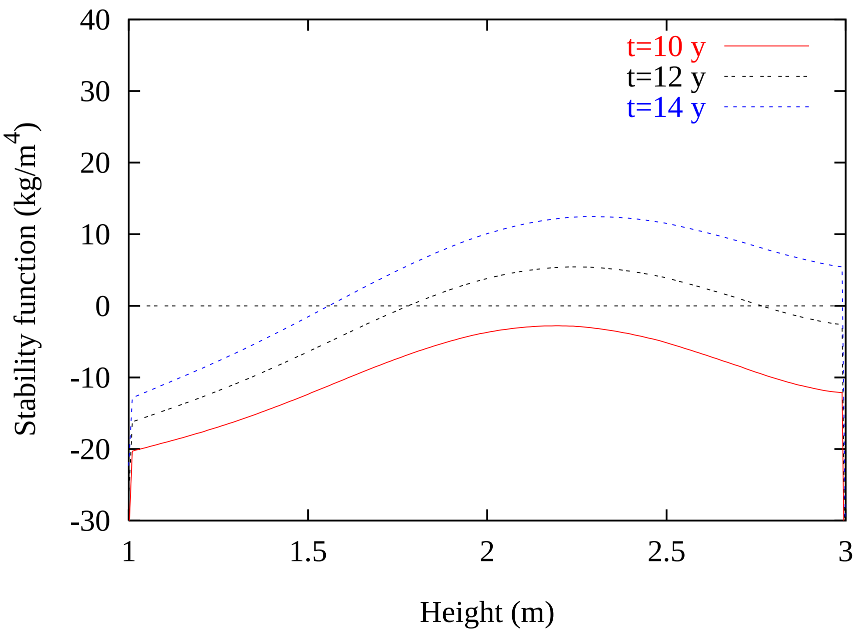

Figure 5: Stability function evolution up to 14 years within the NCZ.

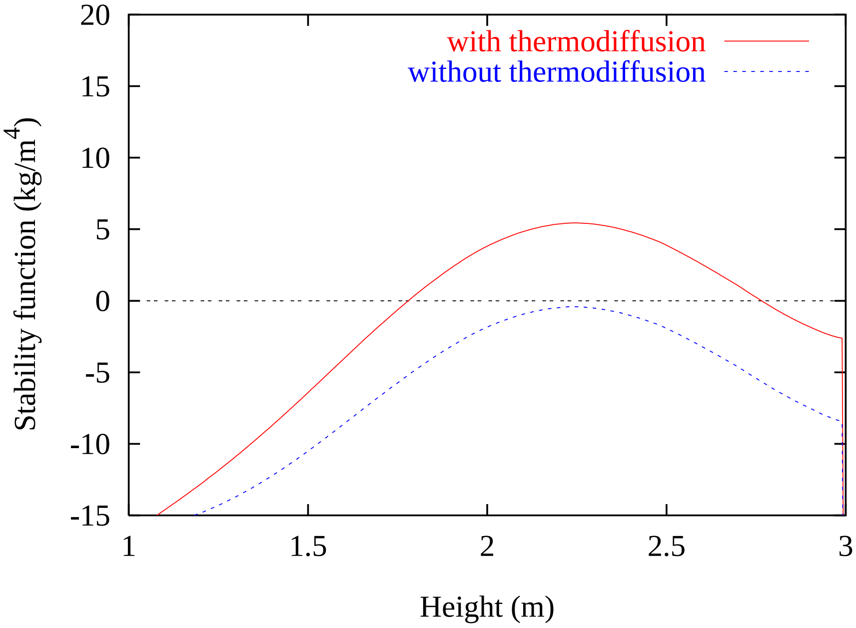

Figure 6: Stability within the NCZ after a period of time of 12 years, when the Soret effect is considered or neglected.

Let us stress that, from the results of the stability analysis, it appears that our approach is not correct on the full simulation time. Indeed after 10 years the salt-gradient becomes instable due to the onset of convective motion. Therefore the concept of steady state, as discussed above, should be reviewed taking into account the development of fast convective processes.

From these preliminary results we can observe that, even if the salt diffusion is a very slow process, in order to ensure solar pond stability for a long period, salt must be added at the bottom, and extracted at the surface, for instance maintaining constant concentrations at the boundaries of the NCZ.

The behavior of the system under these conditions has been simulated with DIFFIN. The flux, concentration, and density at the steady state (which is reached after about 20 years), are shown in Fig. 7.

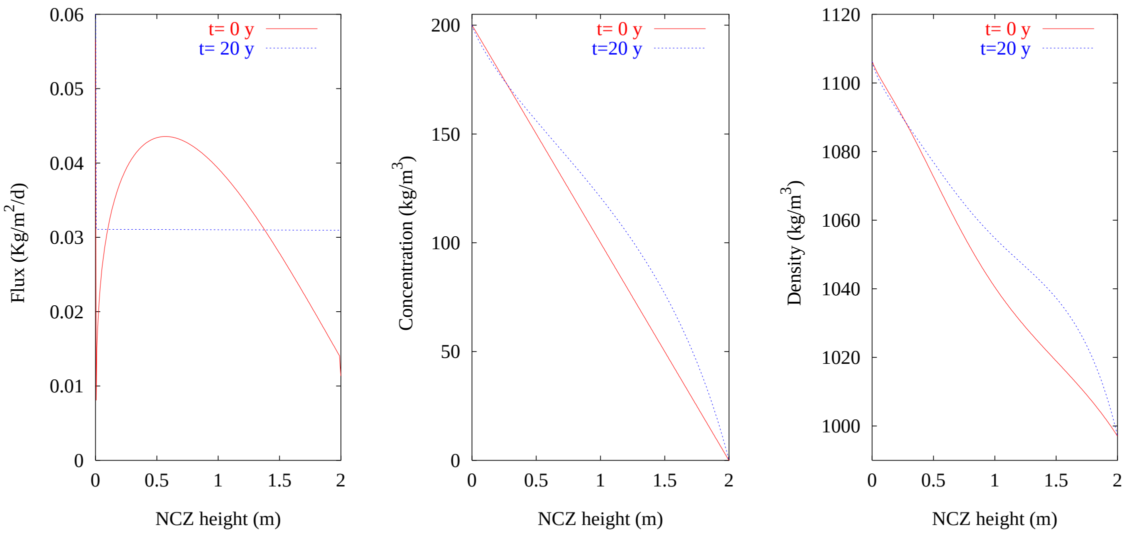

Figure 7: Initial condition and steady state (t=20 years) of flux (left), concentration (center) and density (right), along the height of the NCZ.

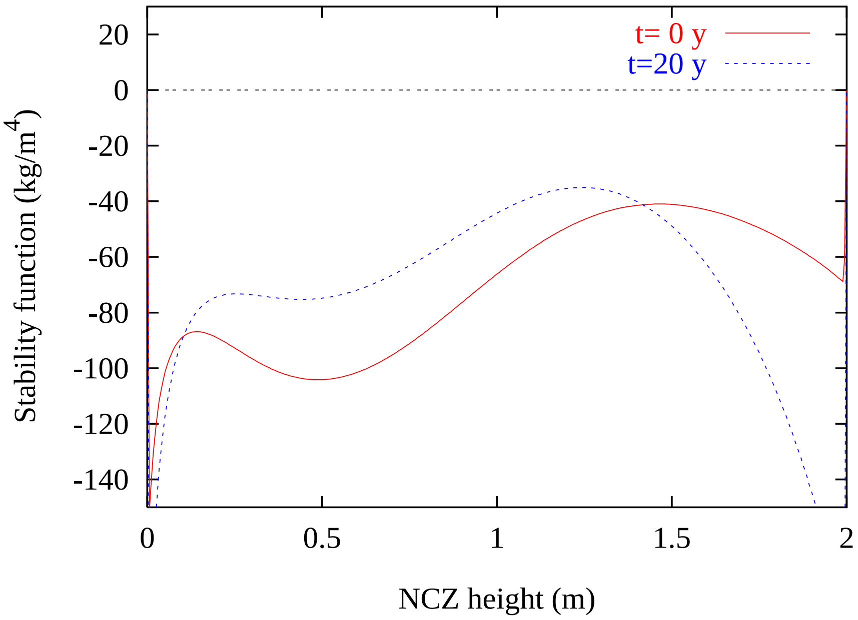

Figure 8: Stability within the thickness of the NCZ at t=0 and at the steady state (t=20 years).

We note that, imposing these boundary conditions (constant concentration), the system we have studied is stable over the full simulation time and therefore our approach is justified. Also, as shown in Fig. 8, at the steady state, the system results still stable following the Rayleigh analysis.

8 Program Keywords

Physical description of the system: namelist &PHYS

- ZMAX = (double precision) total height of the solar pond in m (default 1 m)
- ZDT = (logical), T $\rightarrow$ temperature dependent diffusion coefficient (eq. 31); F $\rightarrow$ not active (default)
- ZDTS = (logical), T $\rightarrow$ temperature and salinity dependent diffusion coefficient (eq. 32); F $\rightarrow$ not active (default). ZDTS=T incompatible with ZDT=T; ZID=T suggested
- D = (double precision) diffusion coefficient (ZDT=F) or D_0 parameter in eq. 31 (ZDT=T), in m^2/day (default $D = 1.20096 \cdot 10^{-4}$)
- ZSOR = (logical), T $\rightarrow$ Soret effect considered, F $\rightarrow$ neglected (default)
- DSOR = (double precision) value of the s coefficient in eq. 40 in 1/K (default DSOR=$2.25 \cdot 10^{-3}$)
- LCZH = (double precision) lower convecting zone hight, in m
- UCZH = (double precision) upper convecting zone hight, in m
- LCZC = (double precision) lower convecting zone concentration, in g/l (or kg/m^3)
- UCZC = (double precision) upper convecting zone concentration, in g/l (or kg/m^3)
- LNCZC = (double precision) concentration in the NCZ on the border with the LCZ, in g/l (or kg/m^3)

- UNCZC = (double precision) concentration in the NCZ on the border with the UCZ, in g/l (or kg/m^3)
- LCZT = (double precision) lower convecting zone temperature, in °C
- UCZT = (double precision) upper convecting zone temperature, in °C
- W0 = (double precision) solar power density, in Watt/m^2/sec
- XK = (double precision) thermal conductivity, in Watt/m/K
- BCOE = (double precision) b coefficient in equation 36
- ZTVAR = (logical), T $\rightarrow$ time dependent temperature profile and time start (t=0) at first january; F $\rightarrow$ constant temperature profile (default)

Printing control: namelist &PRT

- ZPRT = (logical), T $\rightarrow$ verbose printing; F $\rightarrow$ (default)
- NW = (integer) number of time values for which all information are printed on data files

Numerical integration: namelist &NUM

- TMAX = (double precision) total simulation time
- NSTEPT = (integer) number of time steps
- NSTEPZ = (integer) number of steps for the z variable
- ICCL = (integer) LCZ boundary condition: 1 $\rightarrow$ zero flux, 2 $\rightarrow$ constant concentration (see text)
- ICCU = (integer) UCZ boundary condition: 1 $\rightarrow$ zero flux, 2 $\rightarrow$ constant concentration (see text)
- IDCL = (integer) LCZ behavior: 1 $\rightarrow$ only diffusive; 2 $\rightarrow$ diffusive for one time step followed by a convective averaging of concentration

- IDCU = (integer) UCZ behavior: 1 $\rightarrow$ only diffusive; 2 $\rightarrow$ diffusive for one time step followed by a convective averaging of concentration
- ZID = (logical) T $\rightarrow$ switch on the iterative solution of the non linear equations obtained when the diffusion coefficient depend on the temperature and salinity (ZDTS=T); F $\rightarrow$ non iterative solution (default). ZID=T allowed only with ZDTS=T.
- ZIS = (logical) T $\rightarrow$ switch on the iterative solution of the non linear equations for the Soret Effect (ZSOR=T); F $\rightarrow$ non iterative solution (default). ZIS=T allowed only with ZSOR=T.

Output files

- **temp.dat**: z(i),T(i)
- **diffusiv.dat**: z(i),D(i) or z(i),(D(i,j),j=1,nw) if ZID=T
- **mass.dat**: t(j),mass(j),(mass(j)-mass(1))/mass(1)*100
- **conc.dat**:z(i),(c(i,j),j=1,nw)
- **dens.dat**:z(i),(ρ(i,j),j=1,nw)
- **sali.dat**:z(i),(S(i,j),j=1,nw)
- **rayan.dat**:z(i),(r(i,j),j=1,nw)
- **flux.dat**:z(i),(J(i,j),j=1,nw)

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