A Multi-Component Chemistry-Based Model for the Dead Sea

Modifications to the 1D Princeton Oceanographic Model
A Multi-Component Chemistry-Based Model for the Dead Sea:
Modifications to the 1D Princeton Oceanographic Model

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Executive summary

The Dead Sea is a severely disturbed ecosystem, greatly damaged by anthropogenic intervention in its water balance. During the 20th century, the Dead Sea level dropped by more than 25 meters, and presently (2006) it is at about 420 meters below mean sea level. Over the last decade the average rate of water level decline is ~1 m/yr, while salt accumulates at the bottom of the lake at a rate of ~0.1 m/yr. Accordingly, lake volume decreases by some 700 million cubic meters annually. Due to the high density of the Dead Sea brine, this volume translates to an annual freshwater deficit of about 850 million cubic meters. The negative water balance of the lake is mainly due to the diversion of water from its catchment area by Israel, Jordan, Syria and Lebanon, as well as the result of the industrial activity in the southern basin of the Dead Sea, which at its current level would otherwise be dry. In 2002 Israel and Jordan jointly announced their interest in stopping the water level decline and the deterioration of the surrounding infrastructure by constructing a Red Sea - Dead Sea conduit (RSDSC) that will pipe water from the Red Sea to the Dead Sea. The proposed project includes also a desalination plant that will utilize the 400 meter elevation difference between the Seas. In 2005 Israel, Jordan and the Palestinian Authority submitted to the World Bank terms of reference (TOR) for a "Feasibility Study - Environmental, Technical and Economic, and Environmental and Social Assessment". This TOR puts forward, among others, the environmental concerns associated with the proposed RSDSC project. On January 10 2006 the World Bank announced that steps towards the realization of the feasibility study would take place in 2007.

The qualitative impact of seawater mixing in the Dead Sea has been described in several publications of the Geological Survey of Israel (GSI), suggesting that the inflow of seawater (or reject brine after desalinization) into the Dead Sea will have a major impact on its limnology, geochemistry and biology. During the filling stage, to a level to be decided upon by the concerning parties, the water column will become stratified with a relatively diluted upper water layer. The salinity and density of this water are difficult to predict as they will be a function of numerous parameters such as depth of stratification, rate and timing of seawater discharge, rate of evaporation, water turbidity and more. When the desired level is reached, seawater will continue to be discharged to the lake so as to keep pace with evaporation and maintain a stable water level. Once stratification develops, the salts derived from the seawater will accumulate in the upper water layer. Consequently, the composition, salinity and density of the upper layer will change with time. Halite (NaCl-table salt), which currently precipitates from the Dead Sea, will cease precipitating, while the mixing between the calcium-rich Dead Sea brine and the sulfate-rich seawater will result in
gypsum (CaSO$_4$·2H$_2$O) precipitation. It is not known at what rate these gypsum crystals would sink to the bottom of the lake and whether it will lead to whitening of the surface water. Dilution of the surface water will probably result also in microbial blooming whose duration is not known. The lower water layer is likely to develop reducing conditions, including bacterial sulfate reduction and presence of hydrogen sulfide (H$_2$S), similar to the conditions that prevailed in the Dead Sea prior to its overturn in 1979. The entire water column is expected to re-mix when the density of the upper water layer will equal that of the lower waters. In spite of the large volume and high salinity of the Dead Sea relative to that of the inflowing water, over the long run the composition of this unique lake will change.

In order to correctly evaluate and quantify the long-term processes expected to take place in the Dead Sea following seawater inflow, it is necessary to develop a limnological model for the Dead Sea that comprises all parameters that determine the behavior of the lake. The model will thus help determine the extent to which the project is feasible, and the optimal conditions for its implementation. If the RSDSC will materialize, the model may become a valuable tool in the operation of the conduit, enabling the operator to predict the behavior of the lake for the long and short-term and thus assist in the determination of appropriate operational policy.

The significance of the model lies in its ability to correctly simulate the evolution of the water stratification as a function of time, under different inflow rates and volumes at different water compositions and temperatures. However, in addition to the general challenge of modeling a lake, modeling of the Dead Sea dynamics and seawater mixing is a highly challenging task as the lake has several unique features which have not been modeled before. Among these are the large range of salinities and densities, the lake's unique composition, and the precipitation of salts from the water body. Modeling is further complicated by the need to simulate mixing of freshwater and seawater in the Dead Sea, because such mixing imposes a large range of salinities, densities and compositions, which rarely exist in nature, and for which the existing limnological/oceanographic models are not tuned to run. Thus, new and unique modules must be formulated, coded and incorporated into existing codes which serve as the basis for the Dead Sea model.

The present report summarizes the recent advances in the development of a one-dimensional (1D) limnological model for the Dead Sea (1D-DS-POM) which is being formulated by the GSI, based on the 1D Princeton Oceanographic Model (1D-POM). A major driving force for any limnological/oceanographic dynamic model is the
density differences due to differences in the salinities and temperatures of the water bodies involved. In the Dead Sea however, because of salt precipitation from the brine and mixing with water having different compositions, the density of the resulting brine cannot be determined only from its salinity and temperature. Rather, the new density must be calculated from the chemical composition. Accordingly, as a first step, 1D-POM was modified from a salinity-based to a multi-component chemistry-based model. The new 1D-DS-POM transports and mixes individual ions rather than the bulk salts. The density of the brine is then determined from its chemical composition using the Pitzer approach, modified by Krumgalz for the Dead Sea. This module has been coded and incorporated into the model as a unique equation of state. The calculation of the degree of saturation of the brine with respect to halite or gypsum was written as a separate module, based on the thermodynamic approach of Pitzer and Krumgalz for hypersaline waters. Calculation of the amount of precipitated salts from an oversaturated solution to attain saturation commonly involves a time-consuming numerical procedure. During the course of the work a fast algorithm for the quantitative "removal" of salts from oversaturated brine was developed and implemented into the model. All the thermodynamically-based procedures described above rely on the concentration of the chemical constituents given in molal units (mole/kg H$_2$O). However, mass transport equations (turbulent diffusion) are based on salinity units (gr/kg solution). Thus, we added to the 1D-DS-POM an efficient units transformation module. The forcing of the Dead Sea system (and thus the boundary conditions of the model) are the meteorological conditions above the water. These data have been collected by Israel Oceanographic and Limnological Research from a buoy in the Dead Sea every 20 minutes for over a decade. Calibration of the 1D-DS-POM will be based on the limnological data collected from this meteorological buoy as well as on data collected during bi-monthly cruises to the Dead Sea conducted between 1992 and 2001.

In order to run and calibrate the model, the mass (water and salt) and energy balances of the Dead Sea must first be established independently. These balances were determined based on the existing meteorological and limnological data. Calculations indicate that the annual water inflow to the Dead Sea is about 350 million cubic meters, implying that most water inflow to the lake are the observed surface inflows, with only limited volume that discharges to the Dead Sea below the water surface. The rate of evaporation from the surface of the Dead Sea was found to be ~1.15 m/yr while salt accumulates at the bottom of the lake at a rate of about 10 cm/yr.

Preliminary (pre-calibrated) long-term (50 year) 1D-DS-POM runs indicate that stratification and dilution of the surface water will take place under most scenarios in
which the inflows to the lake are increased. In fact, even if the additional water diverted to the Dead Sea would only compensate for the current water deficit and maintain the level at its current (or future) level, stratification would still develop. Under these scenarios the surface density would continuously decrease over the coming decades. The model further indicates that long-term stratification and decrease in surface salinity and density can occur even while lake level declines, provided that the volume of inflow water is greater than that which evaporates from the surface of the lake. This paradox is explained by the net withdrawal of Dead Sea brine by the chemical industries. Stratification develops under such conditions because the water added to compensate for the brine withdrawal dilute the surface water as it lacks the salts that were withdrawn from the lake.

Biological field experiments are being conducted in experimental ponds in the vicinity of the Dead Sea for over four years. These experiments indicate that microbial blooming, which colors the brine in greenish to brownish hue, can occur in the Dead Sea when the brine is diluted by 10% or more of seawater. Increased dilution leads to enhanced blooming while the supply of phosphate, which is the limiting nutrient in the Dead Sea brine, results in particularly strong blooming. Long-term (up to 3 years) experiments showed that blooming, once initiated, may last for a long duration without further addition of phosphate. It is however not clear why such prolonged bloomings were not recorded in the history of the lake. The biological experiments suggest that microbial bloomings in the Dead Sea are likely to accompany the RSDSC. Their extent would be greatly determined by the salinity of the surface water which, assuming the blooming is not desired, should be kept as high as possible.

The expected impact of seawater mixing in the Dead Sea on the limnology of the lake, corroborated by the initial 1D-DS-POM runs as well as the biological field experiments, and their ramifications, underline the need for a further in-depth study of the RSDSC. Among others, this study should include the calibration and detailed scenario-building by the 1D-DS-POM as well as the formulation of 2D and 3D models which should provide insights into the long-term spatial evolution of the Dead Sea.
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1. Introduction

The Dead Sea is the lowest surface on Earth and as such is also a terminal lake. It is the saltiest natural water body on the planet. Over the last forty years the Dead Sea water level has dropped by over 25 meters and currently (year 2006) water level is at 420 meters below mean sea level (-420m). The average rate of water level decline over the past decade is over one meter a year. This decline is due to water diversion from the lake's drainage basin by Israel, Jordan, Syria and Lebanon as well as due to the industrial activities in the lake's now-dried up Southern basin.

The construction of the Red Sea – Dead Sea Conduit (RSDSC) to convey seawater from the Red Sea to fill the Dead Sea has been proposed by the governments of Jordan and Israel as a possible solution to the declining Dead Sea water level. The plan also includes a desalinization plant to be built in the vicinity of the Dead Sea, whereby the 400 meter elevation difference between the Seas will be utilized; the reject brine will be diverted to the Dead Sea and the potable water distributed between Jordan, Israel and the Palestinian Authority (P.A.). Yet, before implementing such a project it is important to provide forecast for the evolution of the lake if the plant is implemented. It must be understood that diverting seawater or concentrated seawater after desalinization (i.e. reject brine) to the Dead Sea is not similar to freshwater inflow (Gavrieli et al., 2005) and the impact of introducing huge volumes of seawater to the lake must be established in advance. Among others, the mixing of these two distinct waters is bound to lead to chemical reaction (i.e. gypsum precipitation) and on the long run will change the composition of the lake. In addition, restoring the DS level to past elevation, even by freshwater, will lead to the stratification of the water body and environmental changes that cannot be fully quantified. Stratification that develops due to seawater inflow poses additional questions: What would be the rate of accumulation of sea-salts in the epilimnion (upper water column)? what will be the composition, temperature, and appearance of the epilimnion and surface water? will there be biological blooming unknown in the DS? what would be the rate of evaporation from the surface water? and many other questions. Overall, it must be established that the changes that will occur due to the RSDSC will not lead to environmental changes and damages that surpass those that currently take place in the Dead Sea and its surrounding.

Over the last few years the Geological Survey of Israel (GSI) has been engaged in research and studies towards the formulation of a dynamic limnological model for the DS which would provide a long term forecast for the evolution of the lake with and without seawater or freshwater inflows. In additional, research is underway to understand the potential biological blooming in the diluted surface water as well as the kinetics of gypsum precipitation. On the long run it is our desire to incorporate all these parameters into the limnological model in order to attain the best possible...

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modeling forecast for the lake. The time frame for the evolution of the Dead Sea that we wish to examine is on the order of decades. Clearly, with such time frame in mind, the model is not aimed at providing detailed daily or monthly changes in the lake, but is to provide future trends and quantitative description of the long term changes in the water column structure and composition.

This report summarizes much of the GSI activities over the past two years in conjunction with the RSDSC. As outlined in this report, the uniqueness of the DS poses some challenging and practical as well as scientific problems. The strategy taken by the GSI in developing our understanding of the mixing between DS and SW is to thoroughly establish the scientific baselines, identify and determine the existing unknowns and finally calibrate a model with all available data and insights into the dynamics of the Dead Sea. This strategy has often resulted in somewhat slow progress in our modeling effort. However, it must be understood that once the model is run under different seawater inflow scenarios the validity of the output cannot be verified as no such large scale experiment has ever been done. Thus, thorough understanding of the Dead Sea system and minimization of the unknowns are a must, allowing us to confidently proceed with the formulation of the model.

2. Energy and mass balances for the Dead Sea

Despite the numerous studies of the Dead Sea and its surroundings, major unknowns about the DS hydrology/limnology still exist. Among these are the energy and mass balances of the lake. In order to calibrate the limnological model and later develop scenarios for the future of the lake, these balances must be established independently of the model. Furthermore, the RSDSC project is greatly dependent on the evaporation from the lake which should enable continuous seawater or reject brine discharge. If the volumes that can be conveyed to the lake are not clearly defined, planning of the project is impaired. Furthermore, it has been suggested that large volumes of groundwater discharge into the DS from the surrounding aquifers due to the decline in its water level (Salameh and El-Naser, 1999). According to this, raising or even stabilizing the lake level would result in decreased groundwater inflow, thereby requiring additional inflow of seawater to achieve the desired rise in the water level.

Existing estimations of the water balance of the Dead Sea are widely variable, reflecting the unknown subsurface groundwater inflows and rate of evaporation. During the course of the present study, these unknowns were determined through the establishment of mass (water and salt) and energy balances for the Dead Sea. This approach combines the extensive meteorological and limnological data base collected at the Dead Sea during the years 1992-2001 by the Hebrew University, Israel Oceanographic and Limnological Research Ltd. and the Geological Survey of Israel. It is independent of any assumption regarding the rate of evaporation or water inflow.
volume. Yearly balances were calculated for the years 1996-2001, during which our region experienced drought and the Dead Sea was characterized as monomictic, i.e. experienced yearly stratification and overturn.

The heat of evaporation was calculated using the Bowen’s approach, as part of the total heat balance. Together with the measured hydrographical quantities, these provide constraints on the total inflows to the Dead Sea. Given the estimates of surface inflows, it is now possible to estimate also the subsurface inflows (i.e. subsurface inflows = total inflows minus surface inflows). The total annual inflows (surface and subsurface) were found to be in the range of 265-365 million cubic meters (MCM), while the evaporation rate is ~1.15 m/yr. Accordingly, the subsurface inflows, deduced from the minimum estimate of surface inflows are thus less than 60 MCM/yr. A higher subsurface inflow is not possible as it requires a higher evaporation rate, for which there is no source of energy flux (Appendix I). Finally, the salt mass balance indicates that salt precipitates and accumulates at the Dead Sea floor at a rate of ~0.1 m/yr.

The results of this study, which constitutes a major advance in our ability to model the Dead Sea, were published as a scientific paper in Water Resources Research. The manuscript, as published there, is presented in appendix I.

3. Formulating a 1D model for the Dead Sea

Formulating a dynamic limnological model for the Dead Sea is a highly challenging task. The dynamics of any water body is primarily dictated by density differences (aside from winds) and these are therefore the basis for the modeling of such systems. Density differences in natural systems commonly do not exceed few per cent, and are often much smaller, yet are sufficient to drive ocean circulations and lead to currents, stratifications etc. In contrast, the difference between the density of freshwater that discharges to the Dead Sea (or the future seawater inflow) and the Dead Sea brine is greater than 20%. Such a huge density difference is seldom found in other natural systems (and does not exist in marine systems) and the dynamic mixing of such a water body has never been modeled.

Additional unique features of the Lake include its Ca-Chloride composition. Currently, halite precipitates from the brine, resulting in a continuous change in the brine’s composition. Thus a simple equation of state that correlates the salinity of the brine with its density must also take into account the changing composition of the lake. The change will be much more pronounced once seawater mixes in the DS. Dilution of the surface water will result in discontinuation of halite precipitation, but the supply of sulfate from the seawater will lead to gypsum precipitation. The density of the epilimnion will thus be a function of its composition and temperature, which
will depend on the mixing ratio, rate of evaporation and the amount of gypsum precipitation from the mixture.

Our strategy in formulating the dynamic limnological model for the DS is to adopt open codes that are within the public domain and are in wide use by the international community, and to modify them to fit the DS. However, the features outlined above necessitate that the code will include parameters, such as chemistry, which are commonly not included in transport modeling, and that some of the fundamental assumptions in the models will be re-evaluated, tested and sometime replaced by new in-house modules. It must be emphasized that no data exists for calibrating the model with seawater inflow. Calibration of the model must therefore be based on a different setting, namely the dataset available from the present conditions of the DS in combination with our new insight into the mass and energy balances of the lake. Our data set spans the years 1992-2001 and includes data on the stratification of the water column between 1992 and 1995, which developed following the exceptional rainy winter of 1991-92. During this winter huge volumes of freshwater inflowed to the lake and diluted the surface water of the Dead Sea. These data are of utmost importance since no other continuous data for the development and destruction of long term stratification of the Dead Sea exists.

For the model to be applicable also for seawater inflow, it must be based on sound thermodynamic and hydrodynamic foundations and it must be calibrated with minimum empirical unknowns and assumptions, while every parameter has to be examined for its validity and sensitivity. Much of our efforts over the past two years were towards establishing these. Only when the model is well calibrated and verified will we be able to examine various operational scenarios for the RSDSC, involving mixing of seawater in the Dead Sea.

The open code which the 1D Dead Sea model is based on is the 1D Princeton Oceanographic Model (1D-POM). This open code can be downloaded from:

http://www.aos.princeton.edu/WWWPUBLIC/htdocs.pom/indexOLD.html

The turbulent closure scheme of the code was simplified as outlined below. All the external, mostly unique modules written for the modeling of the Dead Sea were incorporated into the code (Fig. 1). Below we summarize our progress in formulating and encoding these unique modules, and the rational behind each. In the future these modules will be modified to allow their integration into 2D and possibly 3D models. This will be done once we have completed the calibration and the scenario-building of the new 1D-DS-POM (1D-Dead Sea-Princeton Oceanographic Model).
Fig. 1: Schematic representation of the new multi-component chemistry-based 1D-DS-POM and the interaction of the various modules developed for the model with the central code and with each other. The algorithm and coding of all modules were done in the GSI. The turbulent closure in the basic 1D-POM was also modified.

Initial un-calibrated 1D-DS-POM runs were carried out in order to verify that each module is well integrated and that the modules work in harmony. The results of these runs and their implication are discussed in the last section describing the formulation of the model.

3.1. Vertical turbulence closure

Ocean and limnological models use various turbulent closure schemes for parameterization of subscale mixing and macroscopic heat and mass turbulent transport. POM model utilizes the Mellor-Yamada closure (1982) that expresses vertical turbulence transport coefficients for heat \((K_H)\) and mass \((K_M)\) in terms of turbulent kinetic energy \((q^2)\), turbulent length scale \((L)\) and stability factors \((S_H, S_M)\) respectively:

\[
K_M = q \cdot L \cdot S_M \\
K_H = q \cdot L \cdot S_H
\]

Following the Mellor-Yamada closure (1982), the stability factors are calculated as a function of the Richardson number (Fig. 2). The Richardson number \((R_i)\) is the ratio of the potential to kinetic energy, and is a measure of the stability of stratification:

\[
R_i = \frac{L^2}{q^2} \frac{g}{\rho} \left( \frac{\partial \rho}{\partial z} \right)
\]

where \(\rho\) - the density of the brine, \(\frac{\partial \rho}{\partial z}\) - its vertical gradient and \(g\) - gravity acceleration.
In our modified 1D-DS-POM, we utilized the exponential decay of turbulent kinetic energy with depth, described by the Ekman layer (Rubin and Atkinson, 2001), to describe the depth dependent turbulent kinetic energy ($q^2$):

$$q^2 = A \cdot \exp\left(-\frac{z}{H}\right)$$

This modification of the turbulence energy distribution includes two model tuning parameters: 1) the characteristic depth, $H$, which controls the depth of stratification and 2) turbulent kinetic energy, $A$, of the uppermost layer. Model calibration for these parameters would be carried out against the depth of the thermocline, developed annually between 1995 and 2001, and for which temperature profiles are available.

3.2. Incorporation of mass and energy balances into 1D-POM

The various energy balance terms were incorporated in the model in line with the energy balance described in Lensky et al., 2005 (Appendix I). Year-long runs covered a full annual cycle of the monomictic Dead Sea water column. Only crude calibration was made at this stage in order to verify that the model can correctly depict the behavior of the monomictic Dead Sea. The runs, which begin in winter with homogeneous water column, depict the development of stratification during spring, the heating of the upper water column and its increasing salinity during summer, and
the water column overturn and destruction of stratification during autumn. The runs
included input of water inflows (determined from the water balance calculations) and
the detailed meteorological data (wind, radiation, relative humidity) available from
the meteorological buoy which is maintained on the Dead Sea by Israel
Oceanographic and Limnological Research Ltd. Initial runs were made for year 1998,
for which there are minimum data gaps. Some multi-year, long term un-calibrated
runs are discussed at the end of this report. Future runs will include multi-year runs,
using the data set from 1991-2001 and 2004-present. These runs will be used to
calibrate the model, once all the required modules have been developed, coded and
incorporated into the model.

3.3. Salt precipitation and its effect on the timing of overturn

The 1D-POM was used to determine the significance of modeling salt precipitation
from the water column. The equation of state for the Dead Sea used in these runs was
determined by Anati (1997). Runs begin in winter with a homogeneous water column
having salinity of 277 g/Kg. All runs include annual inflow of 350 MCM of
freshwater, and account for pumping and end brine discharge of 525 MCM/yr and 240
MCM/yr, respectively, by the chemical industries.

Two test-cases are compared: a) No salt precipitation, which results in rise in salinity
due to evaporation from the upper water layer. b) salinity-threshold, identical
conditions to the former run but salinity is not allowed to exceed 278.5 g/kg; when
model output results in higher salinity, the excess salt is "precipitated" from the brine,
leaving it with salinity of 278.5 g/kg. Fig. 3 compares the surface salinity derived
from the two runs. As expected, in runs in which salt precipitation is not included, the
salinity of the surface water (Fig. 3a), from which evaporation takes place, reaches
higher values than in runs that include the salinity threshold. The salinity of the
former reaches values that have never been encountered in the DS and are considered
unrealistic. This high salinity results in earlier overturn of the water column, identified
by the sudden decrease and increase in surface and deep water salinities (Figs. 3a and
3b, respectively). Additionally, water levels and temperatures differ significantly from
those obtained from the no salt precipitation run (Fig. 4). As expected, at the end of
the one-year runs, when the water column is fairly homogeneous, the overall salinity
in the no salt precipitation runs is higher than in the salinity-threshold run. In addition
the temperature and water level at the end of the two runs differ, indicating the
interdependence between salinity and the dynamics of the system.

While we acknowledge that the model is not fully calibrated, these sets of runs
demonstrate the importance of salt precipitation in the modeling of the DS. Timing of
overturn, water temperature, salinity and water level are all inter-related with salt
Fig. 3: Salinity of (a) surface water and (b) at 100 m depth, derived from the salinity-based 1D-POM runs over one year with and without salt precipitation. The latter is based on a threshold salinity of 278.5 g/kg. Runs begin on 1.1.98 with a homogeneous water column and are based on the 1998 meteorological data. Note the higher salinity at the end of the run with no salt precipitation.
Fig. 4: Modeled a) surface temperature and b) water levels derived from one year runs of the salinity-based 1D-POM. Runs begin on 1.1.98 with a homogeneous water column and are based on the 1998 meteorological data. Note the higher surface temperature and lower water level at the end of the run with no salt precipitation.
precipitation. Our results emphasize the importance of correctly modeling the timing and the amount of salt that precipitates from the DS. This can only be done by incorporating a thermodynamic module into the code. This enables to calculate the degree of over-saturation with respect to the salts involved, and then determining the amount that needs to be "precipitated out" from solution to re-attain saturation. Such calculations further require that the chemical composition of the brine (i.e. individual ion concentrations), and not its salinity (i.e. mass of total salts/mass of brine) is tracked and recalculated throughout the runs, as described in the following section.

3.4. Salinity-Based vs. Multi-Component models

Incorporating thermodynamics into the code required major modification. As a first step, the model must be changed from the standard oceanographic modeling approach of a "salinity-based model", which follows a single parameter as a representative of the composition of the water, to a "multi-component model" which traces the change in the individual ions in solutions. This modification will also enable to follow the significant change in the composition of the DS brine, once seawater is introduced to the lake.

The salinity-based 1D-POM model was modified so that the mass transport module, which commonly calculates the transport (mixing) of salinity and temperature, is now activated for each of the major individual ions under consideration. The new code is hereafter named 1D-DS-POM. We included only the major ions which impact the salinity and density of the brine and/or are constituents of the salts presently precipitating or are expected to precipitate from the DS upon mixing with seawater. The ions included are thus: Na, K, Ca, Mg, Cl, Br, HCO$_3$, SO$_4$. We note that at this stage we assume HCO$_3$ to represent the total alkalinity although in fact in the Dead Sea some 2/3 of it is borate.

To the best of our knowledge, no similar multi-component model was ever formulated for oceanographic/limnological systems. The new 1D-DS-POM now traces and records the composition of the 8 major ions in the DS and seawater systems. The units used are those of salinity, i.e. the concentration of the individual ions in solution recorded as (gr ion)/(kg solution). Such concentration units allow activating the existing transport module of the 1D-POM for every chemical component separately.

3.5. Switching between Molality and Salinity units

Thermodynamic calculations which allow the determination of the degree of saturation with respect to a certain salt (e.g. halite NaCl or gypsum CaSO$_4$·2H$_2$O) and the amount that needs to be precipitated to attain saturation, are based on molality
units, i.e. mole/(kg H₂O). As outlined above, in the multi-component model we no longer follow the salinity of the brine but the individual concentration of the ions in salinity units. The 1D-DS-POM must therefore include modules that enable conversion back and forth between these units. The algorithm developed for this purpose (Appendix II) was encoded and incorporated into the multi-component 1D-DS-POM. The code was then checked by running it "blankly", whereby no use is made of the calculated molalities. The resulting output of salinity, water level and temperature were similar to those obtained with a run that did not include these calculations of concentrations-molalities-salinities (Figs. 3-4).

3.6. A new equation of state

The most recent equation of state (EoS) for the Dead Sea, which was established by Anati (1997), correlates the density of the brine with its temperature and salinity. This approach is identical to that taken for seawater, which is valid over a small range of salinities and compositions. In fact, Anati notes that his equation will have to be re-evaluated every few years as the composition of the brine changes due to halite precipitation.

The densities that our DS model needs to determine span beyond the linear mixing between DS (\(\rho \approx 1.24\) gr/cc) and seawater (\(\rho < 1.04\) gr/cc). It should account for densities as low as those of freshwater to the highly concentrated (up to 500 gr/L) and hot (42°C) end brines discharged to the lake by the chemical industries in the southern basin of the Dead Sea. In addition, evaporation from the mixtures and the increased concentrations, as well as changes in compositions due to gypsum precipitation must also be accounted for. Finally, we intend to model the evolution of the lake over the coming decades with no seawater inflow. Under this scenario the DS density is expected to rise beyond its current value, while the composition of the lake will continue to change as halite precipitates from the brine.

To calculate the densities included in the range of composition described above we adopted the approach described by Krumgalz et al., (1982a). This approach makes use of the Pitzer equations for the calculations of the thermodynamic properties of hypersaline brines and is based on the composition of the brine as given in molality units. Appendix III provides more details as to the calculation method. The equations and empirical data on which these equations are based were encoded and incorporated into 1D-POM. Calculated densities derived from chemical compositions were then compared with densities calculated separately using the original code developed by Prof. Krumgalz (personal communication, 2005). These densities were found to be identical.
3.7. Thermodynamics

Incorporation of chemistry in oceanographic or limnological modeling is usually aimed at following nutrient availability for biological and environmental purposes (Cole and Wells 2002; Eckert et al. 2002; Romero et al. 2002). These components however are not fully coupled with hydrodynamic modeling of the system, as they do not influence the water density. This is not the case in the hypersaline Dead Sea system, which is saturated with respect to evaporitic minerals. These, mainly halite, currently precipitate from the brine and thereby change the composition of the Dead Sea and its density. Halite will cease to precipitate from the Dead Sea upon mixing of seawater and the dilution of the surface water. However, a new salt, gypsum, will precipitate instead. Further evaporation of the mixture will lead at some late stage of operation of the RSDSC to the precipitation of halite as well (Gavrieli et al., 2005). Thus **there is a need to include a thermodynamic module** that determines the saturation state of the mixture with respect to the relevant salts. If any of these salts is found to be oversaturated in the brine, the correct amount of salt needs to be "precipitated" from the water to re-attain saturation. The amount of salts that precipitates over time must also be recorded as it accumulates at the bottom of the lake, leading with time to rise in the elevation of the seafloor. As noted above, the density of the solution after it precipitated its salts must then be re-determined through the equation of state. To the best of our knowledge no model exists that incorporates thermodynamic calculations and salt removal.

The saturation degree (saturation index) of a salt with composition $X_nY_m\cdot kH_2O$ (X-Cation and Y-Anion) is defined as:

$$SI = \frac{a_X^n \cdot a_Y^m \cdot a_{H_2O}^k}{K_{sp}}$$

Where:  
$a_{X,y}$: Activity of the ions in the solution, $a_{H2O}$ – water activity;  
$K_{sp}$: Thermodynamic solubility product of the salt

The activity of an ion in a solution is defined as:

$$a_X = \delta_X \cdot m_X$$

Where :  
$\delta_X$ is the ion activity coefficient  
$m_X$ is the concentration of the solution in molality (defined as moles/Kg $H_2O$).
It should be recalled that the chemical thermodynamics of hypersaline systems of high ionic strength is more complicated than that of diluted systems and must account for all possible pair- and triple-ionic interaction in the brine. Thus, determining the activity coefficients of the ions that precipitate as halite or gypsum (Na, Ca, Cl, SO₄) requires numerous computations. The up-to-date approach for dealing with such high ionic strength solutions is the 30 year old Pitzer approach (Pitzer 1973; Pitzer 1975). The modification of this approach for the Dead Sea system and its derivatives was developed by Krumgalz et al (1982b, 1995, 2000, 2001). The principals of these calculations are somewhat similar to those used for the determination of the EoS.

The calculation method described by Krumgalz et al. (1982b) and Krumgalz (2001) was coded as an independent module which was then incorporated into the 1D-DS-POM. The method involves numerous calculations which when first coded were found to be highly expensive in terms of computer-time. It should be noted that the thermodynamic calculations need to be done every few time-steps. Since the new module needs also to work with 2D and 3D models, which have many more nodes and require shorter time steps, it was of utmost important to optimize the computation time. This was done by minimizing duplicate computations which are often required when calculating the activity coefficients of the individual ions, as well as for the calculation of the EoS.

Fig. 5 presents the calculated year long (year 1998 as in previous runs) change in the density of the surface brine and its degree of saturation with respect to halite (DSH). The run was made with the 1D-DS-POM including the new EoS calculated from the chemical composition of the brine. Note the decrease in DSH and density during the summer as a result of summer heating and their increase during the autumn cooling. On day 282 overturn takes place and DSH and density drop due to mixing with the lower waters. The run does not include salt precipitation (once the brine attains saturation; DSH=1).
Fig. 5: DSH and density of surface water calculated by the 1D-DS-POM for year 1998. The model is based on multi-component mixing and the new equation of state. Input data are the relevant meteorological data and updated inflows and energy balances. Note the decrease in DSH and density during the summer as a result of summer heating and their increase during the autumn cooling. On day 282 overturn takes place and DSH and density drop due to mixing with the lower waters. The run does not include salt precipitation (once the brine attains saturation; DSH=1). Precipitation of halite impacts on the density of the surface water and therefore on the timing of overturn (Figs 3-4).

3.8. Quantitative Salt Precipitation

During model runs, once over-saturation has been established, the model will have to "precipitate" the appropriate amount of salts to re-attain saturation with respect to this salt. Effectively, this implies that the correct quantities of the appropriate ions making up the salt should be subtracted from the relevant ion molal concentrations in the brine. In addition, the amount of salt that precipitates from the brine and accumulates at the bottom of the lake must be recorded. The latter is then translated into volume of salts that raises the seafloor and therefore impacts on the water level of the lake.

The computation time of the thermodynamic module, which requires numerous calculations, is relatively long. Thus, we decided to avoid its repeated use for the calculation of the amount of salt that needs to be precipitated out from the solution once oversaturation was attained. In order to achieve this, we developed a linear approximation for the change in the degree of saturation due to small change in composition (Appendix IV). The underlying assumption in our algorithm is that because the model runs with short time steps, high over-saturation does not develop...
between them. According to our approach, once over saturation is identified, the code determines the derivative of the oversaturation as a function of changing ion concentration. Based on this derivative, the code then calculates the amount of salt that needs to be removed from the solution to re-establish saturation. The approach thus assumes a linear derivative over the small change in the degree of saturation as a function of the small change in the ionic concentrations. This approach saves the iterations usually required by the thermodynamic calculations.

Fig. 6 presents calculated (but still not fully calibrated) surface salinity and water level for a one year (1998) run of the 1D-DS-POM, including the new equation of state and salt precipitation. Also included is an identical run with no salt precipitation. Fig. 6 should be compared with Figs 3-4 which describe runs with the salinity-based 1D-POM code. As outlined above (section 3.3.), in runs with no salt precipitation the water column overturns at higher salinity. The final salinity is also higher as compared with the salt precipitation runs. However, unlike in Figs. 3-4 which describe a salinity threshold for the onset of precipitation, the salinity of the surface water in the multi-component run with salt precipitation is no longer constant. Rather it reflects salt precipitation which is determined thermodynamically and is a function of the composition and temperature of the brine at any given moment.

3.9. 1D-DS-POM scenario runs (non-calibrated)

To verify that all the above-described modules were properly integrated in the model and correctly interact with each other as well as with the basic 1D-POM code, several long term (50 years) hypothetical scenarios with different freshwater inflow volumes were run and compared. As the code is not yet fully calibrated, and in order to avoid confusion and misinterpretation of the model output, we did not run it with seawater inflow. Thus, the importance of the current long-term model outputs lies in the general trend observed for the response of the lake to the different inflow volumes while the exact results (e.g. water level, salinity, composition, temperature) are of lesser importance.

Input data in all long-term runs were the 1998 meteorological data, repeated every year. All runs assume the continuation of operation of the potash industries on the shores of the lake, which includes pumping of some 525 MCM/yr of Dead Sea brine and the discharge of 240 MCM concentrated end brines to the lake. Runs begin in 1998 with freshwater inflow volume of 350 MCM/yr, which is maintained until year 2020, when the inflow volume is changed. The runs then continue for additional 30 years with different but constant freshwater input volumes, ranging between no inflows (0 MCM/yr) and 1500 MCM/year.
Fig. 6: a) Calculated surface salinity and b) water level from one year runs based on the multi component 1D-POM with and without thermodynamic salt precipitation.
Fig. 7 presents the results of water level change over the 50 years runs. During the first 20 years water level continues to decline at approximately present day rate. Following the hypothetical blockage of all inflow volumes in year 2020, the rate of water level drop is enhanced, in line with the expected response of the lake. In contrast, introduction of some additional 800 MCM/yr to the lake (i.e. total freshwater inflow of 1150 MCM/yr) stabilizes water level, while higher inflow volumes lead to rising water levels.

**Fig. 7:** Calculated long-term water levels from 1D-DS-POM runs with various freshwater inflows. All runs begin with inflow volume of 350 MCM/yr which continues until year 2020, when a new inflow volume is introduced. In all runs the potash industries pump 525 MCM/yr of Dead Sea brine and discharge 240 MCM/y of concentrated end-brines.

Fig. 8 presents the change in surface and bottom layer densities for these runs. As long as the present conditions are kept constant, surface density continues to rise, and the annual monomictic behavior of the lake is maintained. However, when additional water inflow is allowed into the lake to stabilize lake level, long term stratification develops. Once stratification is established, the upper water column becomes progressively less saline. In turn, as more brine is pumped by the potash industry from the concentrated lower water column, its thickness slowly decreases.
Fig. 8: Calculated long-term a) surface and b) near-bottom densities from 1D-DS-POM runs with various freshwater inflows. Note that stratification and dilution of the surface water develop also with inflow volumes that result in a relatively constant water level (1300 MCM/yr) and even in slow water level decline (1100 MCM/yr). During stratification, the density of the deep brine rises due to the industrial end brines that sink to the lower water layer (thus, runs with 1100-15000 MCM/yr appear as a single line in Fig. 8b)
Long term stratification and decrease in surface salinity occurs also when the inflow volumes are increased beyond present day volumes, but are still insufficient to stabilize lake level. This paradox is explained by the net withdrawal of Dead Sea brine and salts by the chemical industries. In the model, this pumping is done from the concentrated lower water column. Through their activities, these industries withdraw both salt and water from the lake. The water added to compensate for the brine withdrawal dilutes the surface water because it lacks the salts that were withdrawn from the lake. It is important to note that by the end of the run, after 30 years of stabilized level, the density of the upper water layer is less than that which existed in the Dead Sea when it was stratified in the 1960, and density continues to decline. Even lower densities may be expected if the Dead Sea level is to be raised. Note once again that the code is still not calibrated and therefore deviations from the results presented in Figs. 7-8 are to be expected.

4. Biological experiments

Blooming of micro-organism in the Dead Sea could have ecological and esthetic impacts, including changes in the energy balance of the Dead Sea (increased heat absorbance). At this stage, biology is not included in the 1D-DS-POM, but as better understanding of the biological aspects of the RSDSC is gained, we will attempt to incorporate them into the 1D-DS-POM code. To this end, the GSI initiated and coordinates a study on the expected impact of the RSDSC on the microbiology of the Dead Sea. The study is done in collaboration with Prof. Aharon Oren from the Hebrew University, Jerusalem, who is a world leading microbiologist specializing in saline environment in general and the Dead Sea biota in particular, and the Research Department of the Dead Sea Works Ltd (Dr. J. Lati, Mr. M. Kohen and Mr. M. Aharoni) which also provides the site for our experimental pools. Dr. J. Gavrieli, a microbiologist from Tami Research Institute, is involved in the research as a representative of the industry.

The initial findings of our study, which began in 2002, were summarized and published in a paper in Journal of Marine Systems (Oren et al., 2004). The main goals of the study that has been ongoing since then are:

1. To define the boundary conditions in terms of salinity and extent of dilution that determines whether or not microbial blooms may be expected to occur. This is important because it has been previously established that the main factors that determine the development of microbial blooms in the Dead Sea (the green alga *Dunaliella* and red halophilic Archaea of the family *Halobacteriaceae*) are the dilution of Dead Sea water with less saline water, as the Dead Sea in its present state is too saline to support microbial blooms. This conclusion was based on the monitoring of the biology of the Dead Sea in the last 25 years (massive blooms in
1980 and in 1992, which followed the formation of relatively diluted upper water layers in those particularly rainy winters), on laboratory simulations, and on simulations in mesocosms in Beth HaArava (1984-1985) and Sedom (from the summer of 2002 onwards, Oren et al., 2003 and references therein). On the basis of the data collected thus far, it is predicted that the rate of microbial development and the extent of the microbial blooms to be expected in the future will depend on the final salinity of the upper water layers, as determined by the amounts of Red Sea water to enter the lake, the mode of mixing, and also any additional fresh water that may enter the lake in the future during winter rain floods.

2. To simulate sustained blooms and to examine their properties. Analysis of the data collected during the natural microbial blooms (1980-1982 and 1992-1995) have shown that blooms of the unicellular green alga *Dunaliella* appear rapidly, but are also subject to rapid decline. However, the community of red halophilic Archaea that subsequently develops at the expense of organic material produced by the algae from inorganic carbon, using energy supplied by the sun, may remain present for long time periods. To examine the longevity of such blooms under controlled conditions we have set up long-term experiments at the experimental mesocosm pond facility in Sedom

The results of this study have been submitted for publication in Hydrobiologia, and are included in a GSI report (Oren et al., 2005). Appendix V is a slightly modified version of the text submitted for publication.
5. Summary

Over the past 3 years the GSI has formulated the multi-component chemistry-based 1D-DS-POM, which is based on the salinity-based 1D-POM. The new code includes mass transfer of the individual chemical constituents, a new equation of state that is based on the chemical composition of the water or brine, a thermodynamic module and a salt precipitation module. The new code will simulate the long-term evolution of the Dead Sea water column, including changing water level, development of stratification, changing densities and chemical composition, and halite and gypsum precipitation under present conditions or during seawater inflow. However, prior to such simulation, we need to carefully calibrate the model. This will be done using the existing meteorological and limnological data that span over the years of 1992-2001 as well as more recent data (2004-2006). The data from 1992-1995, a period during which the Dead Sea was stratified due to the exceptional rainy winter of 1991-92, would be a critical calibrating tool that would allow us to test whether the code correctly depicts the development and destruction of stratification. Once the 1D-DS-POM is well calibrated we will begin "introducing" seawater and examining various operational scenarios for the RSDSC.

This report outlines the development of the new multi-component salinity-based 1D-DS-POM for the Dead Sea. The difficulties encountered in modeling the Dead Sea and the extra care taken in encoding the unique modules for the Dead Sea are discussed, along with the changes introduced to the salinity-based 1D-POM. These careful procedures will be continued as we will proceed to develop a 2D code (and possibly a 3D code), which will be based on the same new modules.

At this stage the code does not include the biological aspect. This aspect could be of a major importance due to its ecological and esthetic aspects as well as its impact on the energy balance of the lake (the turbid water from the growing micro-organism results in increased heat absorbance). As we develop better understanding of the biological aspects of the Dead Sea, we will examine the means by which biology can be incorporated into the code.
6. References


A Multi-Component Chemistry-Based Model for the Dead Sea


Appendices
Water, salt, and energy balances of the Dead Sea

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[1] The Dead Sea is a hypersaline terminal lake experiencing a water level drop of about 1 m/yr over the last decade. The existing estimations for the water balance of the lake are widely variable, reflecting the unknown subsurface water inflow, the rate of evaporation, and the rate of salt accumulation at the lake bottom. To estimate these we calculate the energy and mass balances for the Dead Sea utilizing measured meteorological and hydrographical data from 1996 to 2001, taking into account the impact of lowered surface water activity on the evaporation rate. Salt precipitation during this period was about 0.1 m/yr. The average annual inflow is 265–325 × 10^6 m^3/yr, corresponding to an evaporation rate of 1.1–1.2 m/yr. Higher inflows, suggested in previous studies, call for increased evaporation rate and are therefore not in line with the energy balance.


1. Introduction

[2] Since the first half of the 20th century, the level of the lowest place on Earth, the Dead Sea, has declined by over 20 m [Gavrieli and Oren, 2004], and since 1996 the average rate of water level drop is about one m/yr. The negative water balance of this unique terminal lake is due to diversion of freshwater from its drainage basin, mainly from water which in the past reached the lake through the lower Jordan River (Figure 1). Yet, despite the environmental impact associated with this decline and the regional and international discussions which aim to resolve and manage the Dead Sea, the water balance of the Dead Sea is not well constrained. The least known parameters in the balances are the evaporation rate and subsurface water inflow. This balance will be crucial for the feasibility study and planning of the proposed “Peace Conduit” project, which aims to convey seawater from the Red Sea to the Dead Sea thereby stabilizing its level [Gavrieli et al., 2005].

[3] Reliable determination of the water balance of hypersaline lakes in general and that of the Dead Sea in particular are more complicated than similar freshwater bodies due to two major factors.

[4] 1. The first is difficulty in determining the amount of evaporated water due to reduced water activity and rate of evaporation: Evaporation from brine surface is less than that from a freshwater surface because the dissolved salts lower the free energy of the water molecules and hence the saturation vapor pressure above the brine. The activity coefficient of water (H_2O) in the brine, β, represents the ratio between vapor pressure above a brine surface and vapor pressure above a freshwater surface at the same temperature [Stumm and Morgan, 1981]. The activity of freshwater is β = 1 by definition, while in hypersaline brines β < 1 (for the present Dead Sea composition, β ~ 0.67).

Accordingly, the rate of evaporation from such water bodies is not equivalent to that from freshwater under similar conditions [Salhofer et al., 1985, 1987; Steinhorn, 1991].

[5] 2. The second factor is difficulty in determining the net water deficit: The decline in the water level of a hypersaline chemically-saturated lake which precipitates salts does not represent the true change in the volume of the lake because the accumulation of the salts effectively raises its floor. The water deficit is therefore larger than it appears from simple level changes. In the Dead Sea, halite (NaCl) began to precipitate in 1979 [Steinhorn, 1983], and since then, continues to precipitate. The rate of accumulation has been estimated to be several centimeters per year, from chemical considerations [Gavrieli, 1997].

[6] To resolve the long-term evaporation rate and water balance of the Dead Sea, we adopt the energy budget method, which is considered the preferable technique for long-term monitoring [Winter et al., 2003]. A somewhat similar but simplified approach was applied to the Dead Sea by Stanhill [1994] and Neumann [1958] utilizing a limited data set. We first present a formulation for the simultaneous determination of the energy, water and salt balances for hypersaline lakes. This approach requires reliable meteorological and limnological data. Using detailed data that accumulated from a buoy in the center of the Dead Sea since 1992, we evaluate annual inflow, rate of evaporation
Figure 1. Location map. Major freshwater inflow: Jordan River (a), En Fesh‘ha springs (b), and Amon-Mujib (c). Dead Sea brine is pumped from location d to the evaporation ponds and the rejected concentrated end brine is diverted back into the Dead Sea at location e. The locations of the meteorological and hydrographic stations are EG100 (g) and EG320 (h). Sedom (i) is located within the evaporation ponds.

and rate of salt precipitation. Figure 2 presents a flowchart for the methodological approach with reference to sections in this article, main equations, figures, and tables.

2. Hydrographical Setting of the Dead Sea

The Dead Sea is a terminal hypersaline lake (salinity \(\sim 277 \text{ g/kg}\)) with extremely high density (\(\sim 1240 \text{ kg/m}^3\) at 23°C). The present (2005) volume of the Dead Sea is \(\sim 132 \text{ km}^3\), with surface area of \(\sim 625 \text{ km}^2\), maximum depth of \(\sim 300 \text{ m}\) and surface level at \(\sim 418\) meters below mean sea level. It forms the lowest place on Earth, which currently is declining by \(\sim 1 \text{ m/yr}\). At the time of the first in-depth study of the properties of the Dead Seawater column, in 1959–1960, the lake was stratified (meromictic) with the shallow southern basin flooded (today it is the site of industrial evaporation ponds, Figure 1). Somewhat less saline upper water mass (epilimnion) floated over a denser lower water mass (hypolimnion) [Neev and Emery, 1967]. The lower water mass had been isolated for at least several centuries [Steinhorn et al., 1979; Stiller and Chung, 1984], was anoxic and contained \(\text{H}_2\text{S}\). It should also be noted that in the past 40 years, the solar radiation in the Dead Sea Rift Valley in general, and in the Dead Sea in particular, has declined by more than 10% [Stanhill and Cohen, 2001].

In 1976, following the negative water budget and lake level drop, the very shallow southern Dead Sea dried out. With the increase in salinity of the epilimnion, its density increased and the stability of the upper layer that had existed during the meromictic state weakened. This finally led to a complete overturn and homogenization and oxidation of the entire water column in 1979 [Beyth, 1980; Steinhorn et al., 1979; Steinhorn and Gat, 1983]. Since then, the Dead Sea experiences mostly annual stratification and overturns (holomictic regime), while its salinity and temperature continuously rise at overturn and its water level declines [Anati and Stiller, 1991; Gertman and Hecht, 2002]. This trend was discontinued twice, following large freshwater inflow during the particularly rainy winters of 1979/1980 and 1991/1992. These inflows lead to the dilution of the surface water and to the development of a stabilizing halocline that maintained the stratification for 3–4 years [Anati and Stiller, 1991; Beyth et al., 1993]. During holomictic years, stratification develops in spring due to the warming of the upper water layer, or less commonly in late winter due to limited dilution of the water as a result of winter rain floods. During summer months, increased evaporation results in a salinity rise of the epilimnion and the development of a destabilizing halocline. However, stratification is maintained by the stabilizing thermocline (generally located between 25 and 30 m depth). Surface water temperatures reach up to 35°C–36°C, while the

Figure 2. Flowchart for the solution of the mass and energy balances. The dashed frames are the three unknowns, which are solved by a set of the three balance equations.
Figure 3. (a) Surface temperature measured in the Dead Sea at station EG100 (see Figure 1 for location). In 1992 a meromictic period began, following a very rainy winter with unusually high inflow from the Jordan River and other sources. This period ended at the end of 1995 when the lake overturned and began a holomictic period. In the holomictic period the Dead Sea water column overturned every winter, and thus the winter surface temperature represents the whole water column. The interannual temperature rise is 0.2–0.3°C, after Hecht and Gertman [2003]. The low surface temperature during winters of the meromictic period is due to intensive cooling of the epilimnion, while in the holomictic period the whole water body is cooled (about 10 times larger in volume) and thus winter temperature are higher. (b) Averaged quasi-salinity ($\sigma_{25}$) (see text for definition) and temperature of the Dead Sea deep water body (below 100 m). (c) Dead Sea level. Note the surface elevation during the rainy years 1992–1993 and the continuous decrease of the Dead Sea level from 1996 to 2001 at a rate of ~1 m/yr.

temperature of the water mass below the thermocline remains stable in the range of 22–23°C. Overturc occurs following the autumn cooling of the upper water column and the consequent increase in its density. Figure 3a shows the surface water temperature interannual fluctuation during 1992–2001. The surface temperature in winters, when the lake is homogeneous, represents the temperature of the entire water column. During the holomictic years (1996–2001), this temperature increased from winter to winter by 0.2–0.3°C/yr [Hecht and Gertman, 2003]. This trend is compatible with the increase in the temperature of the deep water (deeper than 100 m, Figure 3b). Figure 3b also presents the change in the salinity of the deep water, given in quasi-salinity units ($\sigma_{25}$). The latter was defined by Anati [1997] as the deviation of the brine density at 25°C from density of freshwater. During the same holomictic period, the quasi-salinity of the deep water increased annually by about 0.3 kg/m³/yr [Gertman and Hecht, 2002], corresponding to a salinity increase of 0.24 g/kg/yr. The annual heating and increase in salinity are related to the negative water balance of the lake, as manifested by the annual water level drop during this period (Figure 3c).

[9] Natural water inflows to the Dead Sea during the first half of the 20th century were estimated to be in the range of
1600–2000 × 10^6 m^3 per year [Klein, 1998; Neumann, 1958; Salameh and El-Naser, 1999]. The volume of water reaching the Dead Sea today is substantially lower, with estimates varying between <475 × 10^6 m^3/yr (Table 1) and >1000 × 10^6 m^3/yr [Salameh and El-Naser, 1999]. The difference (>500 × 10^6 m^3/yr) is due to different estimations of the unobserved subsurface inflow. The higher inflow estimation is based on a higher estimation of evaporation rate (2 m/yr, from pan evaporation) [Salameh and El-Naser, 1999]. A much lower evaporation rate, 1.05 m/yr, was estimated for the Dead Sea based on an energy balance for the period of 1980s and 1990s [Stanhill, 1994]. Available standard pan evaporation measurements from Sedom in the southern Dead Sea basin (Figure 1), are difficult to use to resolve the evaporation rate from the Dead Sea for three reasons. (1) The lowered water activity in the Dead Sea brine [Salihotra et al., 1985]. (2) Reduced evaporation in an open lake compared to pan [Morton, 1983]. (3) According to Apert et al. [1997], the local conditions at Sedom are different than those in the northern basin, leading to enhanced evaporation. To resolve the evaporation from Dead Sea, we apply the energy balance method on a hydrometeorological data set measured in a buoy located in the middle of the Dead Sea (Figure 1).  

[10] A water balance of the Dead Sea must also take into account the industrial activities in the Dead Sea chemical industries (DSCI, both Israeli and Jordanian). These pump brine from the Dead Sea into evaporation ponds which are located in the otherwise dry southern Dead Sea basin. Here salts precipitate and are harvested by the industry. The concentrated end brine is then returned to the lake with a net water loss of about 250 × 10^6 m^3/yr [Gavioli and Oren, 2004].

[11] Below we present a formulation for the mass and heat balances for salt lakes (section 3). We then apply this formulation to solve for the inflow, rate of evaporation and the rate of salt precipitation in the Dead Sea, based on recently measured meteorological and hydrographical data (section 4).

3. Formulation of the Mass and Heat Balances

3.1. Total Mass Balance

[12] Let us consider a saline lake with bulk density \( \rho \) and total volume \( V_t \) (see Figure 4a and notation section). The total mass of the brine, \( m_b \), is equal to the sum of mass of dissolved salts, \( m_s \), and the mass of fresh water, \( m_w \):

\[
m_b = m_s + m_w = \rho V_t.
\]

[13] With time, several processes change the mass balance (Figure 4b). Evaporation reduces the mass of water in the brine by \( \Delta m_w \), whereas water enters the lake in the form of rivers, runoff, observed springs, and rain and subsurface inflow, the total being \( \Delta m_i \). Salt precipitation reduces the mass of dissolved salts by \( \Delta m_s \). In the case of the Dead Sea, additional uncommon factors need to be included in the balances: the DSCI pump \( \Delta m_p \), of the Dead Sea brine into evaporation ponds, and reject \( \Delta m_r \) of the evaporated end brine back to the lake. The change of the mass of the brine after a period \( \Delta t \) is

\[
\Delta m_t = \Delta m_s + \Delta m_p - \Delta m_i + \Delta m_r - \Delta m_r. \quad (2)
\]

As a result of the above processes, the new mass of the brine after a period \( \Delta t \) is

\[
m_t = (\rho + \Delta \rho)(V_t - \Delta V_r - \Delta V_e), \quad (3)
\]

where \( \Delta \rho \) is the change in density of the brine, \( \Delta V_r \) is the volume of salt precipitated on the sea bottom, and \( \Delta V_e \) is the volume loss as appears from water level drop. Substituting (1) and (2) into (3), and neglecting the second-order terms \( \Delta \rho \Delta V_r \) and \( \Delta \rho \Delta V_e \) that \( \rho \Delta V_r \ll V_t \) and \( \Delta V_e \ll V_r \), yields

\[
\Delta m_r + \Delta m_i - \Delta m_s + \Delta m_p - \Delta m_r = \rho \Delta V_r + \rho \Delta V_e - \Delta \rho V_r. \quad (4)
\]

[14] The equation of mass balance contains three unknowns: mass of water evaporated, \( \Delta m_w \), mass of total water inflow, \( \Delta m_i \), and mass of salt precipitated, \( \Delta m_s \). The total inflow is solved after the rate of precipitation is solved.
from salt balance considerations and the evaporation rate from energy balance considerations (sections 3.2 and 3.3, respectively).

3.2. Salt Mass Balance

[15] The salinity of the brine is the ratio between the mass of dissolved salts and the total mass of the brine:

\[ S = \frac{m_s}{m_i} \tag{5} \]

After a given time \( (\Delta t) \), the new salinity \( S_n = S + \Delta S \) is the ratio between the new mass of dissolved salts and the new total mass of the brine \( m_i - \Delta m_i \). The new mass of dissolved salts is the sum of masses of dissolved salts pumped from the Dead Sea \( \Delta m_{ps} \), end brines that return from the DSCI, \( \Delta m_{sb} \), salts added by the inflow \( \Delta m_{sI} \) and the mass of salt precipitated from the brine \( \Delta m_s \):

\[ S_n = \frac{m_i - \Delta m_i - \Delta m_{ps} + \Delta m_{sb} + \Delta m_{sI}}{m_i - \Delta m_i}. \tag{6} \]

[16] After substitution of (3) in the denominator, substitution of \( m_i = S \cdot m_i \) (5) in the numerator, using the relation \( \Delta V_j = \rho \Delta S / \rho_s \) (volume of salt precipitated is the mass divided by density of the salt) and neglecting the second-order term \( \Delta^2 V_i \), we get

\[ \Delta m_s = \frac{(\rho \Delta V_j - \Delta \rho_s) S_n - m_i \Delta S - \Delta m_{ps} + \Delta m_{sb} + \Delta m_{sI}}{1 - S_n / \rho_s}. \tag{7} \]

[17] This equation can now be substituted into the total mass balance (4). The remaining unknown is then the amount of water evaporated, \( \Delta m_e \), which is solved from energy balance considerations in section 3.3.

3.3. Energy (Heat) Balance

[18] The energy budget for water bodies is generally expressed as [Anderson, 1952]

\[ Q_e = Q_{SN} - Q_{lw} - Q_e - Q_e - Q_{ad}. \tag{8} \]

[19] The energy flux terms \( (\text{W/m}^2) \), shown in Figure 5, are \( Q_{SN} \), net solar radiation incident to the water body; \( Q_{lw} \), net energy lost through the exchange of long-wave radiation between the atmosphere and the body of water; \( Q_e \), evaporative heat flux; \( Q_{ad} \), energy conducted to the atmosphere as sensible heat flux; \( Q_{adh} \), net advected heat into the water body; \( Q_m \), net heat flux, which is the change in energy stored in the body of water. Below we present the different energy flux components in terms of measurable parameters.

3.3.1. Net Heat Flux \( Q_e \) and the Net Adveceted Heat Flux \( Q_{ad} \)

[20] The net heat flux \( Q_m \) or the change in energy stored in the water body, is manifested by the change in the lake’s temperature and mass after the considered period. The net annual energy change for a homogeneous water body, \( E_n \), is related to the mass of the brine, \( m_i \), its surface temperature, \( T_s \), temperature change, \( \Delta T \), and the change in the total mass of the brine, \( \Delta m_i \):

\[ E_n = c_p[T_i m_i - (T_s + \Delta T)(m_i - \Delta m_i)], \tag{9} \]

\[ Q_{SN} \quad Q_{lw} \quad Q_e \quad Q_{ad} \quad Q_m \]

\[ \text{Figure 5. Energy balance. } Q_{SN}, \text{ net solar radiation; } Q_{lw}, \text{ net long-wave radiation; } Q_e, \text{ evaporation and conductive heat flux; } Q_{ad}, \text{ advected heat flux; } Q_m, \text{ net heat flux.} \]

where \( c_p \) is the specific heat capacity of the brine. The net energy is translated to heat flux, averaged for the \( \Delta t \) period over the area, \( A \), of the lake:

\[ \frac{Q_e}{A} = \frac{E_n}{A \Delta t} = c_p \frac{\Delta m_i T_i - m_i \Delta T + \Delta m_e \Delta T}{A \Delta t}. \tag{10} \]

[21] The second-order term, \( \Delta T \cdot \Delta m_e \), is negligible for \( \Delta T \ll T \) and \( \Delta m_e \ll m_i \). The first term is related to the change in mass, or the net advected heat flux, and the second term to other processes that change the temperature of the water body.

[22] The advected heat flux, \( Q_{ad} \), is the net energy gained or lost by a body of water through the ingress or egress of water. Advected masses may result from surface inflow, evaporation and the other terms of equation (2).

\[ Q_{ad} = \frac{\Delta m_i T_i + \Delta m_e T_e - \Delta m_i T_e - \Delta m_e T_e}{A \Delta t}. \tag{11a} \]

[23] Using the definition of \( \Delta m \), (2) and adding and subtracting \( T_e \) from every component in (11a), the advective heat flux is represented in the following form:

\[ Q_{ad} = \frac{\Delta m_i (T_e - T_s) + \Delta m_e (T_e - T_e) + \Delta m_i (T_e - T_s) + \Delta m_e (T_e - T_e)}{A \Delta t}. \tag{11b} \]

[24] Since we are interested in the calculation of the evaporative heat flux, we have to calculate the difference between the net heat flux (10) and the net advective heat flux (11b) rather than calculate them separately. Subtracting \( Q_{ad} \) from \( Q_e \) yields

\[ Q_e - Q_{ad} = -c_p \frac{m_i \Delta T + \Delta m_i (T_e - T_s) + \Delta m_e (T_e - T_s) + \Delta m_e \Delta T}{A \Delta t}. \tag{12} \]

3.3.2. Net Solar Radiation \( Q_{SN} \)

[25] The net solar short-wave radiation penetrating into the water, \( Q_{SN} \), is calculated from the solar radiation measured above the lake surface, \( Q_S \):

\[ Q_{SN} = \alpha \cdot Q_S. \tag{13} \]

where \( \alpha \) is the fraction of radiation that penetrates into the water surface [Payne, 1972; Ryan and Harleman, 1973].

3.3.3. Net Long-Wave Radiation \( Q_{lw} \)

[26] The net long-wave radiation is the difference between the upward infrared radiation emitted by the water
3.3.4. Evaporative Heat Flux \( Q_e \)

The heat flux of evaporation is proportional to the difference between saturation vapor pressure above the saline lake, \( e_{sat} \), and the atmospheric vapor pressure, \( e_a \) (15):

\[
Q_e = f(w) (e_{sat} - e_a) \tag{17}
\]

The vapor pressure of a brine, \( e_{brine} \), is lower than that of freshwater, \( e_{sat} \), by a factor \( \beta \), which is the water activity [Salikatra et al., 1985]:

\[
e_{brine} = \beta \cdot e_{sat}(T) \tag{18}
\]

The wind function, \( f(w) \), accounts for the effect of air convection above the water surface on the rate of evaporation. This is the least known parameter in the energy balance, thus the Bowen’s approach [Anderson, 1952; Bowen, 1926] is widely used to eliminate the wind function out of consideration, as described below.

3.3.5. Conductive (Sensible) Heat Flux \( Q_C \)

Conductive heat flux, \( Q_C \), is driven by the temperature difference between the water surface and the atmosphere; it can be either a source or a sink of heat for the water body, depending on the difference between the temperatures:

\[
Q_C = c_p \frac{P}{1000} f(w)(T_e - T_a) \tag{19}
\]

where \( P \) is the atmospheric pressure (mbar) and \( c_p \) is the Bowen’s constant, typically 0.61 mbar°C [Anderson, 1952; Bowen, 1926; Rubin and Aitkinson, 2001]. Equation (19) includes the same wind function, \( f(w) \), as in (17). The use of the same wind function in (19) as in (17), is based on the similarity between heat and vapor transport [Bowen, 1926; Businger, 1973]. This approach allows eliminating the wind function by combining (17) and (19):

\[
Q_e = Q_C \cdot B \tag{20}
\]

where \( B \) is the Bowen ratio:

\[
B = \frac{c_p}{\rho_c} \frac{T_e - T_a}{e_{brine} - e_a} \frac{P}{1000} \tag{21}
\]

and \( P \) is the atmospheric pressure. The conductive heat, \( Q_C \), is now expressed in terms of the evaporative heat, \( Q_e \). Substituting (20) into (18) enables expressing evaporation heat flux in terms of heat flux components:

\[
Q_e = Q_{SN} - Q_{SW} - Q_e + Q_{AD} \cdot \frac{1}{1 + B} \tag{22}
\]

This equation enables calculating the evaporative heat flux based on measurable meteorological and hydrological quantities without the need of the wind function.

3.3.6. Evaporation Rate \( \Delta h_e \)

The evaporative heat flux (22) is related to the rate of evaporation, \( \Delta h_e \) (m/yr) through the latent heat of vaporization, \( L_v \):

\[
\Delta h_e = \frac{Q_e}{\rho_e} \frac{\Delta T}{\rho_c} \frac{Q_{SN} - Q_{SW} - Q_e + Q_{AD}}{1 + B} \tag{23}
\]

where \( T \) is temperature in °C and \( e_{sat} \) in mbar [Barenbrug, 1974].
Note that the density and the latent heat of vaporization refer to the brine. The mass of evaporated water is \( \Delta m_e = \Delta h \rho_w A \).

We now have a set of three equations (4, 7, 23) with three unknowns \( \Delta m_i, \Delta m_e, \Delta m_r \) expressed through measurable data and physical properties of the brine and the atmosphere above it.

4. Application of the Model to the Dead Sea

The solution of the mass and energy balances for the Dead Sea is based on the data set collected by Gemann and Hecht [2002] at the hydrometeorological buoy which was anchored in the Dead Sea (station EG100, see Figure 1 for location) and operated from 1992 to 2001. The data set consists of meteorological and hydrographical measurements and includes air temperature \( T_a \), relative humidity \( RH \), incoming solar radiation \( Q_{\text{S}} \), atmospheric pressure \( P \), surface water temperature \( T_w \) and temperature profile down to 40 m below the sea surface. The data is averaged and recorded every 20 min. The balances are calculated for all data records (every 20 min) and then averaged over each year during the holomictic period 1996–2001. The Dead Sea level is measured on a monthly basis by the Israel Hydrological Service. Hydrographical profiles taken in intervals of two months at the deepest part of the Dead Sea, at site EG320 (water depth ~310 m, Figure 1), provide the vertical distribution of temperature, salinity and density and the annual change in surface temperature (\( \Delta T \)), salinity (\( \Delta S \)) and density (\( \Delta \rho \)) of the bulk Dead Sea (Figure 3b).

During the winters of 1996–2001, the Dead Sea water body was well mixed with homogeneous distribution of water temperature and composition. Therefore the measurements taken at the sampling station (EG-320) in consecutive winters represent the annual variations of the heat stored in the Dead Sea, the salinity of the brine and the total mass of the Dead Sea brine. Yearly balances are calculated based on the meteorological data for the holomictic period 1996–2001. The current situation of very low water inflow into the Dead Sea allows significant simplification of the balances. On an annual basis, the total inflow is less than 1% of the volume of the lake. The low inflow has negligible impact on the salt and heat balances, but is an important component in the water mass balance. The adjacent freshwater Lake Kinneret (Figure 1), which receives relatively large volume inflow, including saline springs, requires a more complex solution of the balances as presented by Assouline [1993].

Below we calculate the balances of the Dead Sea and determine the water inflow, rate of evaporation and mass of precipitated salt for year 1999 (Table 2). The heat and mass balances for this year is the closest to the average annual balances calculated for each year during the holomictic period. The interannual variations of the balances during the holomictic years are discussed in section 4.4.

4.1. Salt Accumulation at the Bottom of the Dead Sea

The observed annual rise in the salinity of the Dead Sea brine (\( \Delta S = 0.24 \) g/kg per year, Figure 3b) is lower than that expected from the negative water balance. This is attributed to the precipitation of salt (halite) from the saturated brine [Gavrieli, 1997]. Using the equation of salt balance (7) and the measured parameters, we solve for the mass of precipitated salts, \( \Delta m_i \). It is useful to express \( \Delta m_i \) in units of volume per unit area. The surface area of the lake, \( A \), is assumed to be constant during a year (\( \Delta A \ll A \)). This enables expressing the masses involved in the mass and salt balances in terms of volume per unit area and density:

\[
\begin{align*}
\Delta m_i &= \rho \Delta V_i = \rho \Delta h_i A \\
\Delta m_e &= \rho \Delta V_e = \rho \Delta h_e A \\
\Delta m_r &= \rho \Delta V_r = \rho \Delta h_r A \\
\Delta m_i &= \rho \Delta V_i = \rho \Delta h_i A \\
\Delta V_i &= \Delta h_i A \\
\Delta V_i &= \Delta h_i A
\end{align*}
\]

(24)

Substitution of (24) into the salt balance (7) yields

\[
\Delta h_i = \frac{(\Delta h_\rho h_\rho \Delta \rho) S_e - h_\rho \Delta S - \Delta h_\rho h_\rho S_e + \Delta h_\rho h_\rho S_e + h_\rho \Delta S_e}{\rho_i - (\rho + \Delta \rho) S_e}
\]

(25)

The contribution of inflow to the salt balance is very low due to their relatively low volume and salinity \( (S_e < 10 \) g/kg on average) and therefore the term \( \Delta h_\rho h_\rho S_e \) can be neglected. One can argue that the salinity is higher in the unobserved inflow. However, as will be shown below, the volume of unobserved inflow is no more than a few tens of \( 10^3 \) m\(^3\)/yr. Substituting the measured data from Table 2 into the salt balance (25), the calculated rate of salt accumulation at the bottom of the Dead Sea is \( \Delta h_i = 0.10 \) m/yr. Even if we assume Dead Sea salinity for the unobserved inflow, which is probably a wild overestimate, the contribution to the calculated salt layer is <0.02 m/yr. This would have a minor effect on the rest of the balances. The calculated salt precipitation is in the range of previous estimates based on changes in the composition of the brine [Gavrieli, 1997], measurements of samples collected from the bottom [Levy, 1992] and from sediment traps [Still et al., 1997].

4.2. Evaporation

The evaporation rate from the Dead Sea surface is calculated from the energy balance (23). Figure 6 presents the calculated energy balance terms and shows that the largest component in the balance is the forcing solar radiation \( Q_{\text{S}} \). The net long-wave radiation \( Q_{\text{LW}} \) is determined independently from equations (14). Table 2 presents these calculated \( Q_{\text{LW}} \) values for the Dead Sea in 1999, which span over the range of \( 68-108 \) W/m\(^2\). The minimum and maximum values of the evaporative flux \( Q_e \) depend on the maximum and minimum \( Q_{\text{LW}} \) values, respectively (22), as shown in Figure 6. An additional, but relatively minor source of uncertainty in the calculated
evaporation rate derives from the uncertainty in the reflected short-wave radiation (albedo). Under typical conditions of predominantly light winds and relatively smooth sea surface, the average value used for albedo is 6%, i.e., $\alpha = 0.94$ [Payne, 1972; Rubin and Atkinson, 2001; Ryan and Harleman, 1973]. A deviation of 1% from the latter value changes the rate of evaporation by 0.02 m/yr. A similar uncertainty in the calculated evaporation derives from a 0.05°C/yr uncertainty in the measured annual temperature rise of the water. The uncertainty related to the Bowen ratio approach cannot be estimated due to the lack of direct measurements, but, according to McNaughton and Laubach [1998], "...using the Bowen ratio method to calculate surface energy fluxes will usually incur only minor errors."

[29] When incorporating the range of calculated $Q_{sw}$ values from equation (14) into (23), and temperature rise of 0.25°C/yr, the calculated annual evaporation rate varies between 0.83–1.21 m/yr (Figure 7a). However, as discussed below, estimated surface inflow constrain the lower range of the calculated $\Delta h_i$ to 1.1 m/yr. This range is close to the evaporation rates of 1.05 m/yr suggested by Stanhill [1994] based on heat balance calculations, and 1.23 m/yr estimated by Yechiel et al. [1998], but differs significantly from the rate of 2.0 m/yr based on pan evaporation by Salameh and El-Naser [1999].

### 4.3. Water Inflow

[39] Annual water inflow to the Dead Sea are calculated from the mass balance (4) using the salt annual precipitation (25) and rate of evaporation (23). It is useful to reduce (4) using (24) into the following form:

$$\Delta h_i = \Delta h_i + \frac{\rho_v}{\rho_w} \Delta h_i - \frac{\rho_v}{\rho_w} (\Delta h_i - \Delta h_w) + \frac{\Delta h_i - \Delta h_w}{\rho_w} = \frac{\Delta h_i}{\rho_w}$$

(26)
inflow ranges from $265 \times 10^6$ m$^3$/yr, estimated from observations, to $323 \times 10^6$ m$^3$/yr, determined from the calculations. Since the inflow and evaporation are linked through equation (26), this also constrains the minimum evaporation rate to 1.10 m/yr (Figure 7a).

[2] Figure 8 plots the correlation between the hypothetical annual temperature change of the Dead Sea, $\Delta T/\Delta t$ (representing the net heat flux (10)), and the hypothetical annual inflow (representing the mass balance (26)). The different correlations (the inclined lines) derive from the various formulations for the net long-wave radiation. Also included in Figure 8 is the measured annual heating (0.25 ± 0.05°C/yr, the horizontal rectangle). The observed annual inflow range (265–475, Table 2) is plotted as vertical lines. The gray area represents the possible total inflow into the Dead Sea in 1999. The maximum calculated total inflow, $323 \times 10^6$ m$^3$/yr, is obtained when taking the lowest $Q_{lw}$ value (the right inclined line) with an annual temperature rise of 0.25°C/yr. The uncertainty in the temperature rise (±0.05°C/yr) is translated to only ±8 × 10$^6$ m$^3$/yr. Higher subsurface inflow is not possible as it requires a higher evaporation rate, for which there is no source of energy flux.

4.4. Interannual Variations

[3] The calculations presented above for year 1999 were repeated for the other Holocene years 1996–2001 as well. As noted above, the constraint for the minimal total inflow derives from the minimum observed inflow ($265 \times 10^6$ m$^3$/yr). The maximum calculated inflow for each year (Figure 9), is derived from the use of the formulation which yields the lowest long-wave radiation [Efimova, 1961] (see Table 2). The average interannual maximum inflow is $325 \times 10^6$ m$^3$/yr ±10%. This variability is due to the interannual variation in the measured meteorological and hydrographical parameters over and in the Dead Sea.

Figure 6. Energy flux components based on equations (12)–(14) and (20)–(22) and observed data. The highest and lowest estimates for long-wave radiation (from Bignami et al. [1995] and Efimova [1961], respectively) are presented along with the consequent variation in the evaporative and conductive heat fluxes.

Figure 7. Variation in the calculated (a) rate of evaporation and (b) freshwater inflow with respect to the different net long-wave radiation. The different formulations of long-wave radiation (equation (14)) are indicated. Higher estimation of net long-wave radiation relates to less evaporation (equation (23)) and thus less inflow (equation (26)) and vice versa.
Accordingly, the average unobserved subsurface inflow for this period range from zero to a maximum of $60 \times 10^6$ m$^3$/yr.

4.5. Dead Sea at High Water Levels (pre-1950)

During the beginning of the 20th century, the Dead Sea water level was relatively stable and the lake extended also into the shallow southern basin. Here we analyze the Dead Sea balances during this period, assuming steady state conditions [Neumann, 1958]. A rough estimation of the rate of water balance considerations. As a terminal lake under steady state conditions, evaporation equals inflow ($\Delta m_i = \Delta m_e$), and the net heat flux is zero ($\Delta Q_v - \Delta Q_{live} = 0$). The salt contribution entering with the enhanced freshwater inflow and the precipitating minerals were negligible ($\Delta m_s = 0$), and the industrial activity ($\Delta m_i$, $\Delta m_r$) was minimal. Applying the formulation described above ((4) and (23)) under the steady state conditions, it is possible to express the inflow ($\Delta m_i$) as a function of surface temperature and meteorological parameters:

$$\Delta m_i = \frac{\Delta T}{L_e} \frac{Q_{SN} - Q_{SW}}{1 + B}$$

[45] Historical data for the Dead Sea during 1942–1946 are summarized by Neumann [1958]. The surface elevation at that time was $\sim 392$ m below sea level and the lake area (including the southern basin) was $\sim 950$ km$^2$. At that time, the lake was still stratified with a relatively diluted epilimnion. The density of the surface water ranged between 1140–1190 kg/m$^3$. The annual averages include $T_e = 23.6–25.4^\circ$C; $e_o = 15.9–14.1$ mbar and $T_e = 24.7–25.3^\circ$C [Neumann, 1958]. On the basis of the chemical composition [Neev and Emery, 1967] for 1960, the water activity of the surface water was $\beta \sim 0.73$. In the beginning of the 20th century the salinity was even lower with estimated water activity of $\beta \sim 0.8$. The solar radiation in the Dead Sea rift valley was higher by more than 10% than the present radiation [Stanhil and Cohen, 2001]. Using the above ranges, the estimated inflow from energy balance calculations (27) falls in the range of $1550–1750 \times 10^6$ m$^3$/yr. Accordingly, despite the lower average surface temperature, the evaporation rate was 1.6–1.85 m/yr, which is higher than present-day evaporation (1.1–1.2 m/yr). The above derived values for the beginning of the 20th century compare well with previous estimates of inflow ($1580 \times 10^6$ m$^3$/yr [Neumann, 1958]) and evaporation rates (1.57–1.98 m/yr [Stanhill, 1994]) for the same period.

Figure 9. Maximum inflow ($\Delta I_r$) calculated for the different holomictic years (1996–2001), based on the formulation of minimum net long-wave radiation [Efimova, 1961].
[56] The higher solar radiation during the early 20th century has a significant impact on the calculated evaporation rate. Keeping the measured parameters for that period, and using the reduced present-day solar radiation, reduces evaporation rate to 1.35–1.6 m/yr. This means that for the historical inflow and present solar radiation, the surface level of the Dead Sea would be higher and the area would be larger than those of the early 20th century. Thus the increased evaporation rate during the early 20th century should be attributed not only to the higher surface water activity, but also to the higher solar radiation reaching the Dead Sea surface at that period.

5. Summary and Conclusions

[57] The existing estimations of the water balance of the Dead Sea are widely variable and reflect the unknown subsurface water inflow and rate of evaporation. The situation is further complicated by the continuous salt precipitation from the Dead Sea hypersaline brine which raises the Sea bottom, and the industrial activity in the southern Dead Sea basin. The industries pump brine from the Dead Sea into evaporation ponds and discharge the concentrated brines back to the Dead Sea.

[58] We presented here a framework for the calculations of the total inflow and rates of evaporation and salt accumulation in a hypersaline lake with application to the Dead Sea, using energy and mass balance considerations. The application of the formulation to the Dead Sea is simplified since, on an annual basis, the relatively low inflow has very small effect on the salt and energy balances. The annual inflow are much lower than the total volume of the Dead Sea (<1%), while the temperature difference between the inflowing water and the bulk lake is usually <10°C. The mass of salt carried in by such low inflow is negligible compared to the high total salt content of the Dead Sea.

[59] The terms of the energy budget are calculated using meteorological and hydrographical data collected by a buoy located in the middle of the Dead Sea. The data set for the holomictic years 1996–2001 is recorded every 20 min and is the most detailed record of the Dead Sea. The heat of evaporation is calculated using Bowen’s approach that eliminates the poorly constrained wind function from the heat balance. Since we do not have a direct measurement of the net long-wave radiation, we apply existing formulations that rely on meteorological data.

[60] The total annual inflow into the Dead Sea is 265–335 × 10^6 m³/yr, corresponding to evaporation rates of 1.1–1.2 m/yr. The range of values derives mainly due to the variations between different formulations of the net long-wave radiation. A maximum subsurface inflow of 60 × 10^6 m³/yr is deduced from the maximal total inflow and minimal estimate of observed surface inflow (265 × 10^6 m³/yr). Higher subsurface inflow is impossible as it requires higher evaporation rate, for which there is no source of energy.

[61] Salt precipitation rate is 0.1 m/yr (per m²). The accumulation of a salt layer at the bottom of the Dead Sea implies that the net rate of decrease in the lake’s volume (height) is even higher than may be deduced from water level decline. Accordingly, the water deficit of the lake is nearly 690 × 10^6 m³/yr. It should be noted that some 250 × 10^6 m³/yr of this deficit are due to the activity of the chemical industries in the southern basin of the Dead Sea, equivalent to water level drop of ~0.4 m/yr. Thus, without the current industrial activity, lake level drop would be ~0.6 m/yr.

[62] Higher evaporation rate during the early 20th century, when the Dead Sea level was stable at a higher position, is attributed not only to the lower salinity, but also to the higher solar radiation reaching the Dead Sea surface at that period.

[63] To reduce the uncertainties in the mass and energy balances, we intend to add to our meteorological buoy the measurements of the net long-wave radiation over the Dead Sea.

Notation

- $A$: surface area of the Dead Sea.
- $\Delta A$: annual change of the surface area.
- $B$: Bowen ratio.
- $C$: cloud cover.
- $c_b$: Bowen’s constant.
- $c_p$: specific heat capacity of the brine.
- $e_a$: atmospheric vapor pressure.
- $e_{sat}$: saturation vapor pressure.
- $e_{sat,al}$: saturation vapor pressure above the saline lake.
- $F_{in}$: annual energy change.
- $f(w)$: wind function.
- $\Delta h_1$: water level drop.
- $\Delta h_s$: annual precipitation of salt.
- $\Delta h_e$: annual evaporation.
- $\Delta h_f$: annual freshwater inflow.
- $\Delta h_b$: salt precipitation raises the floor of the lake.
- $k_b$: Boltzmann coefficient.
- $L_q$: latent heat of vaporization.
- $m_i$: total mass of the brine.
- $m_f$: mass of fresh water.
- $m_d$: mass of dissolved salt.
- $\Delta m$: mass of water evaporated.
- $\Delta m_i$: mass of water inflow.
- $\Delta m_p$: mass of pumped Dead Sea brine.
- $\Delta m_r$: mass of rejected end brines.
- $\Delta m_d$: mass of dissolved salts.
- $\Delta m_c$: change of the total mass.
- $P$: atmospheric pressure.
- $Q_{AD}$: advective heat flux.
- $Q_c$: conductive heat flux.
- $Q_e$: evaporative heat flux.
- $Q_{lw}$: net long-wave radiation.
- $Q_n$: net heat flux.
- $Q_s$: measured short-wave radiation.
- $Q_{sw}$: net short-wave radiation.
- $RH$: relative humidity.
- $S$: salinity of the brine.
- $S_i$: salinity of the inflow.
- $S_n$: new salinity of the brine.
- $S_r$: salinity of rejected end brines.
- $\Delta S$: change in the salinity of the brine.
- $\Delta t$: time period (year).
- $T_a$: air temperature.
- $T_i$: inflow water temperature.
- $T_r$: reject end brine temperature.
- $T_s$: surface water temperature.
- $\Delta T$: change in surface water temperature.
total volume of the brine.

$\Delta V_b$ volume loss as appears from the Dead Sea level drop.

$\Delta V_s$ volume of salt precipitated.

$\Delta V_p$ volume pumped.

$\Delta V_r$ volume of rejected end brines.

$\Delta V_f$ fresh water inflow.

$\alpha$ fraction of $Q_f$ that penetrates into the water surface.

$\beta$ water activity.

$e$ emissivity of water surface.

$\rho_b$ bulk density of the brine.

$\Delta \rho_b$ changes in the density of brine.

$\rho_w$ freshwater density.

$\rho_h$ halite (solid) density.

$\rho_e$ rejected end brines density.

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Appendix II: Molality (m) – salinity(S) unit conversion

1. From molality (mol/Kg H₂O) to salinity (g/Kg Solution).

Let \( m \) – ion or a dissolved salt molality, in mol/Kg H₂O;

\( \mu \) – the corresponding atomic or molecular weight.

If in 1Kg of H₂O there are \( m \cdot \mu \) grams of dissolved salt and no other salt is dissolved, then the weight of the solution is \( (1000 + m \cdot \mu) \) grams. Accordingly, if in \( (1000 + m \cdot \mu) \) grams of solution there are \( m \cdot \mu \) grams of this salt, than the concentration of the salt, in salinity units (S; g/Kg Solution) is:

\[
S = \frac{m \cdot \mu}{1000 + m \cdot \mu} \cdot 1000
\]

Similarly, if the solution contains \( N \) ions, then the concentration, in salinity units, of the individual ions, \( i \), is:

\[
S_i = \frac{m_i \cdot \mu}{1000 + \sum_{i=1}^{N} (m_i \cdot \mu_i)} \cdot 1000
\]

and the salinity of the solution is:

\[
S = \sum_{i=1}^{N} S_i
\]

2. From g/Kg Solution to mol/Kg H₂O:

Let \( S \) be the salinity in g/Kg Solution. Thus, there are \( S \) grams of salts for 1000-\( S \) grams of water. Accordingly, for 1000 grams of water there are \( x \) grams of salts:

\[
x = \frac{1000S}{1000 - S}
\]

Assuming the salinity is derived from a single salt, then the molal concentration (\( m \)) of this salt is:

\[
m = \frac{x}{\mu} = \frac{S}{\mu} \cdot \frac{1000}{1000 - S}
\]

Similarly, translating the concentration of the individual ions from salinity units (\( S_i \)) to molal units (\( m_i \)) is carried out as follows (\( S \) being total salinity, \( S = \sum_{i=1}^{N} S_i \)):

\[
m_i = \frac{1000S_i / \mu_i}{1000 - S}
\]
This may be written in a more generalized form:

\[ m_i = \frac{S_i}{\mu_i} \cdot \frac{1000}{1000 - \sum_{i=1}^{N} S_i}, \]

where \( N \) is the number of ions in solution.
Appendix III: Pitzer/Krumgalz approach for density calculations of a multi-component hypersaline solution (Equation of State - EoS)

The density of a solution at a given temperature and composition is calculated from Krumgalz et al, 2000, (Eq. (24):

$$\rho_{\text{mix}} = \frac{1000 + \sum_{i=1}^{N} m_i \mu_i}{1000 + \sum_{i=1}^{N} m_i V_i^0 + V_{\text{mix}}^e} \quad (1)$$

Where:
- $m_i$: concentration of ion $i$ in molality (mol/kg H$_2$O);
- $\mu_i$: atomic weight of ion $i$;
- $\rho_0$: density of pure water at the given temperature (Eq. 15, Krumgalz, 2000);
- $V_i^0$: single-ion limiting partial molal volume (i.e. ionic partial volume at infinite dilution);
- $V_{\text{mix}}^e$: excess molal volume of a multiple-solute electrolyte solution.

There are two unknown functions in Eq. (1), $V_i^0$ and $V_{\text{mix}}^e$. The former is calculated from the data provided in Table 2 and Eq. (18) of Krumgalz, 2000. The calculations are based on the equation for thermal dependency of the limiting partial molal volume of Cl$\text{ }^-$ (Krumgalz, personal communication).

The latter ($V_{\text{mix}}^e$) is described by Eq. (8) in Krumgalz, 1995:

$$V_{\text{mix}}^e = A_V \left( \frac{l}{b} \right) \ln (1+b\sqrt{T}) + RT \left[ 2 \sum_c \sum_{a} m_c m_a \left( B_{c,a} + \sum_c m_c z_c C_{c,a} \right) \right] + \sum_c \sum_{a} m_c m_a \left( 2 \Theta_{c,a} + \sum_a m_a \Psi_{c,a} \right) + \sum_a \sum_{a'} m_a m_{a'} \left( 2 \Theta_{a,a'} + \sum_a m_a \Psi_{a,a'} \right) \quad (2)$$

Where: $A_V$ (the Debye-Hückel slope) is given by Eq. (16), Krumgalz, 2000;
- $I$ is the ionic strength of the solution;
- $z_i$ – ionic charge of ion $i$ (a dimensionless integer);
- $b$ – a numeric coefficient, $b=1.2$ kg$^{1/2}$ mol$^{-1/2}$;
- $B_{c,a}^V$ is calculated in Eq. (7) of Krumgalz, 2000: $z_i = \frac{1}{2} \sum_{i=1}^{N} m_i z_i^2 \quad (3)$
\[ B_{e,a}^{V} = \beta_{e,a}^{(0)V} + \beta_{e,a}^{(1)V} g\left(\alpha_1 \sqrt{I}\right) + \beta_{e,a}^{(2)V} g\left(\alpha_2 \sqrt{I}\right) \]  

(4)

Where: \( \beta_{e,a}^{(j)V} \), \( j = 0 - 2 \) are coefficients whose dependencies on temperature for different salts are presented in Krumgalz, 2000, Tables 4-6, and

\[ g\left(\alpha_j \sqrt{I}\right) = \frac{2}{(\alpha_j \sqrt{I})^2} \left[ -1 - \alpha_j \sqrt{I} \exp\left(-\alpha_j \sqrt{I}\right) \right] \]  

(5)

(Krumgalz, 1995, Eq. 13). The coefficient \( \alpha_1 = 2.0 \) for 1:1, 1:2 and 2:1 electrolytes and \( \alpha_2 = 1.4 \) for 2:2 electrolytes; the parameter \( \beta_{e,a}^{(2)V} \) is introduced only in the equations for 2:2 electrolytes. The temperature dependence of \( C_{e,a}^{V} \) for different salts is given in Table 7 of Krumgalz, 2000.

The third term of Eq. 2 above consists of two terms that describe binary mixtures with a common ion. Of all the parameters that describe such interactions, only two are known (Krumgalz, 1995, Table IV) so the second part of Eq. 2 above reduces to:

\[ RT \cdot m_{Na} m_{K} (2 \cdot 1.52E-05 - 6.72E-06 m_{Cl}) . \]

This completes the description of the term \( \nu_{mix}^{ext} \).
Appendix IV: Optimization of computation time for salt precipitation

Three major salts should be considered when modeling the Dead Sea with and without seawater inflow:

1) Halite (NaCl), which currently precipitates from the DS.
2) Gypsum (CaSO\(_4\)\(\cdot\)2H\(_2\)O), which is currently oversaturated in the Dead Sea and is expected to precipitate in massive volumes upon seawater mixing in the Dead Sea.
3) Carnallite (K\(_2\)MgCl\(_3\)\(\cdot\)6H\(_2\)O), which is under-saturated in the Dead Sea but precipitates in the evaporation ponds of the chemical industries in the southern Dead Sea. If the RSDSC is not constructed and Dead Sea salinity continues to rise, carnallite may also begin to precipitate from the more concentrated DS brine.

Determination of the saturation degree of each of the above minerals is carried out using the thermodynamic module of the model, which is based on the Pitzer approach. Once the program identifies that the brine is oversaturated with respect to a given mineral, this mineral is "precipitated" from the brine. Below we outline our approach to the "precipitation" of the salts from the brine which is designed to minimize calculation time.

Upon identification of an oversaturated composition, the program re-calculates the degree of saturation of the salt only once more. The calculation is carried out on the brine from which a predetermined amount of the oversaturated salt was removed \((q)\). The program then calculates the change in oversaturation vs. the change in the concentration of the salt. This slope is then used to determine the amount of salt that needs to be removed from the oversaturated brine to re-establish saturation. Thus, instead of a cycle of iterations that involves repeated subtraction of the constituents (ions) making up the salts and repeated calculations of saturation degree, which is a time consuming process, we calculate the degree of saturation of the salt only once more.

Below we outline the calculation method:

The degree of saturation of salt \(A_\alpha B_\beta nH_2O\) is defined as:

\[
\Omega_{A_\alpha B_\beta nH_2O} = \frac{(m_A \gamma_A)^\alpha (m_B \gamma_B)^\beta a_{H_2O}^n}{K_{SP}} \tag{1}
\]
where A and B are the cation(s) and anion(s) making up the salt, respectively,

\[ m: \text{ the molality of the corresponding ion,} \]
\[ \gamma: \text{ ion activity coefficient,} \]
\[ \alpha_{H_2O}: \text{ water activity in the brine} \]
\[ K_{SP}: \text{ thermodynamic solubility product of the salt (a function of temperature).} \]

Theoretically, salt precipitation should begin when \( \Omega > 1 \). However, in the salt precipitation module, we introduce a small threshold value, \( \xi > 0 \), such that precipitation starts only when \( \Omega \geq 1 + \xi \). By the end of the process, having precipitated \( \Delta m \) molal of salt, saturation should be re-established, i.e. \( \Omega' \approx 1 \).

Let us consider gypsum precipitation. First we calculate the change in the degree of saturation following precipitation of an infinitesimal (known) amount, say, \( q \), of gypsum. That is after the precipitation of \( q \) moles of the gypsum, the molalities of Ca and \( SO_4 \) will change by \( q (=q_{SO_4}=q_{Ca}=1/2q_{H_2O}) \) because of the precipitation. At the same time, the molalities of all components (including Ca and \( SO_4 \)) will change due to the change in the \( H_2O \) content of the brine. Since each molecule of gypsum precipitates with two molecules of \( H_2O \), the change in \( H_2O \) weight for every 1 kg of water is \( 2\Delta m \cdot 0.018 \), where 0.018 is the atomic weight of \( H_2O \) (in kilograms).

Accordingly, the new molal concentrations of Ca and \( SO_4 \) will be:

\[
m_{Ca,SO_4} = \frac{m_{Ca,SO_4} - q}{1 - 2qm_{H_2O}} \tag{2}
\]

While the new concentrations of all other ions in the solution after removal of \( q \) molal of gypsum will be:

\[
m'_i = \frac{m_i}{1 - 2qm_{H_2O}} \tag{3}
\]

Using these new molalities the new saturation degree, \( \Omega' \), is calculated. Using this new value, we define a derivative, \( M \), which describes the change in saturation degree vs. the change in the concentration of the salt:

\[
q = M \Delta \Omega \Rightarrow M = (\Omega - \Omega')/q; \tag{4}
\]

This value is then used to determine the amount of salt (in molality) that needs to be removed from the oversaturated brine to attain saturation:
\[ \Delta m = (\Omega - 1)/M \] \hspace{1cm} (5)

Having determined the amount of hydrated salt that needs to be removed from the brine to attain saturation, the program then calculates the new molalities of all ions, following eqs. (2) and (3) with \( \Delta m \) replacing \( q \).

The calculation for carnallite is carried out in a similar fashion although in this case

\[ \Delta m = \Delta m_K = \Delta m_{Mg} = 1/3 \Delta m_{Cl} = 1/6 \Delta m_{H2O} \]

While for halite

\[ \Delta m = \Delta m_{Na} = \Delta m_{Cl}, \]

and the molalities of the rest of constituents do not change.
Appendix V:

Long-term field simulation of algal and archaeal blooms in the Dead Sea

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**Abstract**

To obtain a deeper understanding of the factors that determine the extent of blooms of algae (the unicellular green alga *Dunaliella*) and halophilic Archaea in the Dead Sea, and to predict the possible effects of the planned Red Sea – Dead Sea water carrier on the biology of the Dead Sea, we performed simulation experiments in 0.9 m$^3$ experimental ponds on the grounds of the Dead Sea Works Ltd. at Sedom, as well as in the laboratory. Laboratory simulations showed that development of *Dunaliella* was possible only when Dead Sea water was diluted with minimally 10 percent (by volume) of Red Sea water. Addition of phosphate was essential for the algae to grow, and growth rates and yields increased with increasing phosphate concentration and decreasing salinity. Field simulations in outdoor ponds showed that development of algae was rapidly followed by development of dense blooms of red halophilic Archaea, which imparted an intensely red color to the ponds. While algal numbers declined after the peak of the bloom had been reached, number of halophilic Archaea and levels of archaeal pigments remained high for periods of up to 2-3 years at least. The results show that a microbial bloom, once formed, can remain present in the Dead Sea for very long times. These observations are important when attempting to predict how the biological properties of the lake may change in the future, and they have important implications for the planning of the Red Sea – Dead Sea water carrier.

**Introduction**

The Dead Sea presents fascinating challenges to the biologist who attempts to understand the biological processes and the limits of life in one of the most extreme environments on Earth. Its waters contain around 340 g l$^{-1}$ of salts, and have a highly unusual ionic composition: divalent cations (1.887 M Mg$^{2+}$, 0.436 M Ca$^{2+}$) dominate over monovalent cations (1.594 M Na$^+$, 0.199 M K$^+$). The anions are 99% Cl$^-$ (6.335 M) and 1% Br$^-$ (0.068 M) (values for 1996). Sulfate concentrations are low (0.005 M), and the brine has a pH of about 6.

Only few microorganisms can live in such an environment. Quantitatively the most important inhabitants of the water column are the unicellular green alga *Dunaliella* – the sole primary producer in the lake, and red extremely halophilic Archaea of the family
Halobacteriaceae. Species first reported from the Dead Sea include Haloferax volcanii (Mullakhanbhai & Larsen, 1975), Haloarcula marismortui (Oren et al., 1990), Halorubrum sodomense (Oren, 1983a), and Halobaculum gomorrense (Oren et al., 1995a). Other organisms have been isolated from the Dead Sea as well, including colorless members of the domain Bacteria, protozoa, and fungi (Oren, 1988; Oren, 2003). Their quantitative importance in governing the biological properties of the lake has never been ascertained.

Systematic monitoring of the algal and prokaryotic communities in the water column of the Dead Sea since 1980 has yielded the following general picture: undiluted Dead Sea water is a too harsh environment even for the best salt-adapted microorganisms. However, exceptionally rainy winters can turn the holomictic regime into a meromictic one with the formation of a pycnocline at depths varying between 5 and about 15 m (Gavrieli & Oren, 2004; Gavrieli et al., 1999). When the surface waters become sufficiently diluted, dense blooms of algae and red Archaea develop in the upper meters of Dead Sea water column. Such blooms were recorded in 1980 (lasting until a renewed mixing of the water column in the end of 1982) and in 1992 (lasting until the end of 1995). During these blooms the density of the biota reached very high values: up to $9 \times 10^3$ and $1.5 \times 10^4$ Dunaliella cells ml$^{-1}$, and up to $2 \times 10^7$ and $3.5 \times 10^7$ archaeal cells ml$^{-1}$ were counted in 1980 and 1992, respectively (Oren, 1983a; Oren, 1985; Oren, 1993a; Oren, 1997; Oren, 1999a; Oren, 2000; Oren & Gurevich, 1993; Oren & Gurevich, 1995; Oren & Shilo, 1982; Oren et al., 1995b). These archaeal blooms imparted a red color to the entire lake. Field observations combined with laboratory simulations have shown that two conditions must be fulfilled for a microbial bloom to occur in the Dead Sea: the upper water layers must become diluted to a sufficient extent, and phosphate, the limiting nutrient in the lake, must be available.

A thorough understanding of the biological phenomena in the Dead Sea and the factors that determine the nature and extent of biological blooms in the lake is of great importance when planning human interference in the properties of the lake. During the past decade the level has dropped approximately one meter per year on the average (Gavrieli & Oren, 2004; Oren & Gavrieli, 2002; Yechieli et al., 1998). This drop in water level is causing severe problems in the area for local infrastructure, tourism, and industrial activities. Currently a proposal is being investigated for the construction of the "Peace Conduit", connecting the Dead Sea with the Gulf of Aqaba (Red Sea). This planned water carrier is intended to counteract the drop in Dead Sea water level, mitigating damaging processes that currently occur in the Dead Sea and its surrounding area. The difference in elevation between the Red
Sea and the Dead Sea (current surface level: -418 m) may be exploited for energy generation and seawater desalination (Gavrieli et al., 2005; Oren et al., 2004; Oren et al., 2005).

The present study, combining laboratory model experiments with simulations in outdoor ponds, was intended to provide answers to two basic questions: (1), what are the boundary conditions with respect to dilution and phosphate concentrations that enable the development of algae in the Dead Sea, and (2), how long may algal and archaeal blooms, once formed, remain present in the lake when limnological conditions will remain constant.

**Methods**

*Field-scale simulation experiments in the experimental ponds at Sedom*

Mixtures of Dead Sea water and Red Sea water were incubated in experimental ponds on the grounds of the Dead Sea Works Ltd. at Sedom. The experimental setup consisted of white plastic tanks (1 x 1 x 1 m; Dolav, Kibbutz Dvir, Israel), buried for 75% in the ground. These tanks were filled with 900 l of mixtures of Dead Sea water (sampled from the channel that feeds the evaporation ponds of the Dead Sea Works Ltd. with water from the northern basin of the lake) and water from the Gulf of Aqaba, purified through a filter of 60-70 cm sand, eliminating particles larger than 20-30 µm. The first set of experiments performed at the site, initiated in July 2002, as well as further details of the experimental setup, have been documented by Oren et al. (2004). The experiments documented in the present paper started in 2002-2003, and are based on two ponds. One pond (“no. 4”) was filled with a mixture of 80% Dead Sea water and 20% Red Sea water, amended with 1 µM KH$_2$PO$_4$ and inoculated with 50 ml of brine from a pond that had developed a bloom of *Dunaliella* and halophilic Archaea in the previous set of experiments. The second pond (“no. 9”) contained a 1:1 mixture of water from ponds no. 9 and 10 from the earlier experiment. These ponds both contained a 70% Dead Sea water – 30% Red Sea mixture and 1 and 10 µM KH$_2$PO$_4$, so that the new experiment was based on brine that had received an equivalent concentration of 5.5 µM phosphate, and started at the high algal and archaeal densities that had developed in the first round of experiments as documented (Oren et al., 2004). The ponds were mixed daily, and their water level was kept constant by adding deionized water every 1-2 days, followed by thorough mixing. In November 2004, an additional portion of 1 µM KH$_2$PO$_4$ was added to pond no. 4. The ponds were sampled once every two weeks for the
determination of the density of the *Dunaliella* population, the halophilic archaeal community density, and the content of algal chlorophyll and archaeal carotenoids.

**Laboratory-scale simulation experiments of microbial development in Dead Sea – Red Sea water mixtures**

To examine in further depth the effect of salinity and phosphate concentration on the development of *Dunaliella* in Dead Sea – Red Sea waters, we set up laboratory experiments in which 100-ml Erlenmeyer flasks were filled with 75 ml portions of Dead Sea water (sampled in July 2005 from a depth of 10 m at the deepest point of the lake 8 km east of Ein Gedi) and filtered Red Sea water as described above. Different concentrations of KH$_2$PO$_4$ were added, and all flasks were inoculated with a culture of *Dunaliella* from the Dead Sea in 80% Dead Sea water – 20% Red Sea water to supply an inoculum of about 500 *Dunaliella* cells ml$^{-1}$. The flasks were incubated at 30 °C under constant illumination (100 µM quanta m$^{-2}$ s$^{-1}$) by white fluorescent tubes. To prevent evaporation and to ensure constant salinity for the duration of the experiment, the flasks were closed with Parafilm. After 25 days samples were withdrawn for microscopic enumeration of *Dunaliella* cells and chlorophyll assay.

**Enumeration of algae and halophilic Archaea**

To count the density of the algal (*Dunaliella*) and halophilic archaeal communities, 50 ml of samples from the experimental ponds were fixed with 1 ml of 37% formaldehyde, previously cleared by filtration through a 0.2 µm pore size membrane filter. Samples were stored at room temperature until analysis, performed within 3-4 weeks.

For the enumeration of *Dunaliella* cells, 2.5-ml portions of fixed samples were supplemented with 0.1 ml of 0.1 N iodine to stain intracellular starch. The samples were then filtered through Millipore filters (25 mm diameter, 5 µm mean pore size, cat. no. SMWP-25). Filters were placed on microscope slides, and cells were counted under a 16x or a 40x objective. A similar procedure was followed for the enumeration of algal cells in laboratory experiments. No prior fixation was used in this case, and variable volumes of water filtered were filtered according to the density of *Dunaliella* in the flasks. Cell numbers were calculated from the average number of cells per field and the field diameter, calibrated with the aid of the grid of a Petroff-Hauser counting chamber (Oren and Shilo, 1982; Oren et al., 1995b). Prokaryotic cells (Archaea and Bacteria combined) were enumerated microscopically using a Petroff-Hauser counting chamber after 5-10-fold concentration by centrifugation (20 min, 12,000 x g). The
relative accuracy of the algal and prokaryotic cell counts was estimated at ± 10 and 20%, respectively.

**Pigment determinations**

The content of chlorophyll and carotenoids in the experimental ponds was determined by filtering 50-ml sample portions through glass fiber filters (Whatman GF/C, 47 mm diameter) within 1 hour after sampling. Filters were kept at -20°C in the dark until further processing within 3-4 weeks. Filters were then extracted overnight in 5 ml methanol/acetone (1:1, by volume). For the determination of chlorophyll in laboratory cultures, 30 ml portions of liquid were filtered through 25 mm diameter GF/C filters, and the filters were extracted in 2.5 ml of methanol/acetone. The extracts were cleared of particles by centrifugation, and their absorption spectra (400-700 nm) were measured in a Cary Varian model E1 scanning spectrophotometer, using the solvent as a blank. Chlorophyll concentrations were calculated, assuming a specific absorption of 73.5 l mg⁻¹ cm⁻¹ at 665 nm.

Archaeal bacterioruberin pigments were quantified based on a specific absorption of 25.4 l mg⁻¹ cm⁻¹ at 496 nm for α-bacterioruberin. A correction was made for the contribution of algal pigments to the total absorbance at this wavelength, as outlined in Oren et al. (2004).

**Results**

Our outdoor simulation experiments in 0.9 m³ ponds show that once a microbial bloom has formed in a Dead Sea – Red Sea water mixture, it can persist for over two years (Figs. 1 and 2).

Figure 1 documents a bloom of *Dunaliella* and halophilic Archaea in a mixture of 80% Dead Sea water and 20% Red Sea water, supplemented with 1 μM orthophosphate. Algal numbers reached values of up to 12,000 cells ml⁻¹ (16 μg chlorophyll liter⁻¹) after 4 months, and then declined to low values. Mass development of algae was followed by the growth of halophilic Archaea, which are heterotrophic microorganisms that develop at the expense of organic compounds produced by the autotrophic algae. We counted up to 65x10⁶ prokaryotic cells ml⁻¹, and their bacterioruberin carotenoids (up to 18 μg liter⁻¹) imparted an intensely red color to the brine. This community remained present throughout the experiment, without any major decline for more than two years. To prove that further algal development was limited
by the availability of phosphate after the initially added phosphate had been taken up by the microbial community and was incorporated in the biomass, we added an additional 1 \( \mu \text{M} \) orthophosphate in November 2004. This addition quickly resulted in a renewed development of *Dunaliella*. A similar long-living microbial bloom was obtained in a pond that had received a mixture of 70% Dead Sea water – 30% Red Sea and 5.5 \( \mu \text{M} \) phosphate (Fig. 2). This experiment was a continuation of an experiment set up in July 2002, documented earlier (Oren et al., 2004). It shows once more that such microbial blooms can be sustained for long periods, in this case for over three years.

The examples shown in Figs. 1 and 2 are part of a more extensive set of experiments in which we examined the effect of different parameters on the timing and extent of microbial development in Dead Sea – Red Sea mixtures. Some of the early experiments have been described in an earlier paper (Oren et al., 2004). Without added phosphate no significant algal and archaeal blooms were observed. Insoluble finely powdered rock phosphate (apatite) did not trigger blooms (not shown).

To further test the boundary conditions that enable the onset of an algal bloom in Dead Sea – Red Sea water mixtures, we set up a laboratory simulation experiment in which different mixtures were supplemented with different concentrations of orthophosphate and an inoculum of *Dunaliella*. After incubation in the light for four weeks, algae developed only when the concentration of Dead Sea water in the mixtures was below 90%, and the rate at which the cells multiplied increased with decreasing salinity of the water mixture. The extent of the algal growth obtained was a function of the concentration of phosphate added (Fig. 3). These results confirm and extend laboratory simulation experiments performed in the early 1980s in which Dead Sea water was diluted with freshwater (Oren & Shilo, 1985).
Discussion

Compared to all other aquatic environments of lower salinity, the Dead Sea is a very simple ecosystem. Higher animals are absent, and protozoa, if they are present at all, do not appear to play a significant role in regulating community densities of unicellular algae and heterotrophic prokaryotes. The main players are one type of primary producer – the alga *Dunaliella*, and several species of halophilic Archaea (Kaplan & Friedmann, 1970; Oren, 1988; Oren, 1997). Figure 4 presents a general model of the biological processes that occur in the aerobic water column of the Dead Sea, the organisms involved, and some of the interrelationships between the biota. This model is based on observations of the dynamics of algal and archaeal communities in the lake, laboratory simulations, as well as field-scale simulations such as documented in the present study.

Undiluted Dead Sea water is too harsh an environment even for *Dunaliella*, the best salt-adapted alga known. Therefore algal blooms, and subsequent mass development of Archaea that live at the expense of organic material produced by the algae, can only occur after dilution with less saline water. Analysis of the biological events following the rainy winters of 1979-1980 and 1991-1992 have provided ample illustration of this (Oren, 1983b; Oren, 1993a; Oren & Gurevich, 1995; Oren & Shilo, 1992; Oren et al., 1995b), as have simulation experiments (Oren & Shilo, 1985; Fig. 3 in the present study). One of the organic compounds produces in massive amounts by *Dunaliella* is glycerol, used by the algae to provide osmotic stabilization. Evidence has accumulated that this glycerol is probably one of the major nutrients used by the halophilic Archaea (Oren, 1993b; Oren, 1994).

Phosphate is clearly the limiting nutrient that governs the extent of microbial blooms in the lake. Inorganic nitrogen is plentifully available in the form of ammonium ions, but phosphate concentrations are low. Stiller & Nissenbaum (1999) and Nissenbaum et al. (1990) reported dissolved phosphate levels of about 1 µM. Due to the difficulty in performing high-precision chemical analyses in the presence of molar concentrations of other interfering salt it cannot be ascertained to what extent this value indeed represents the true concentration of biologically available phosphate. Furthermore, little information has been obtained on the spatial and temporal variation in the concentration of dissolved phosphate in the Dead Sea water column. In any case, the dramatic response of the *Dunaliella* community to phosphate addition in laboratory and field-scale simulation experiments unequivocally proves its
importance as a key nutrient that determines the properties of the Dead Sea as an ecosystem. Following uptake by the algae, the phosphate becomes fixed in the algal and archaeal biomass. Addition of more phosphate provides the opportunity for renewed algal growth (Fig. 1).

The simulation studies documented in Figs. 1 and 2, as well as in an earlier publication (Oren et al., 2004), show that mass development of *Dunaliella* is generally followed by a rapid decline. The causes of this decline are still poorly understood. Following the 1992 spring bloom of the alga, the cells were observed to form cyst-like structures, possibly zygotes, which sank to the bottom (Oren et al., 1995b). Evidence has been obtained that such thick-walled cysts serve as the inoculum that enables rapid development of *Dunaliella* in the Dead Sea as soon as the upper water layers become diluted by freshwater floods (Oren, 1999b; Oren & Ben-Yosef, 1997). We never observed formation of such cysts in the experimental outdoor ponds.

While algal blooms, both in the Dead Sea itself and in the pond simulation experiments, were always of limited duration, the Archaea remained present for very long times both in the lake (Oren, 1983b; Oren & Gurevich, 1995,) and the experimental ponds were after 2-3 years as brightly red colored as when the bloom first started (Figs. 1 and 2). It has been suggested that the halophilic Archaea in the Dead Sea can to some extent use light energy absorbed by the retinal pigment bacteriorhodopsin as an energy source for maintenance (Oren, 1983c; Oren & Shilo, 1981). Little is known about the factors that remove archaeal cells from the Dead Sea water column. Overturn of the water column with mixing of the Archaea-rich upper layer with the lower water masses has been a major factor in the decrease in prokaryote densities following the 1980-1982 and 1992-1995 blooms (Oren, 1985; Oren, 1988; Oren, 2000; Oren, 2003). Bacteriophages may also be involved in regulating archaeal community densities in the lake, as direct electron microscopic examination revealed large numbers of phage-like particles (Oren et al., 1997). However, their true impact on the community dynamics has never been ascertained (Oren, 1999b).

Understanding the factors that trigger the development of microbial blooms and determine their longevity is important in the planning of the Red Sea – Dead Sea water carrier (Gavrieli et al., 2005; Oren et al., 2004; Oren et al., 2005). A permanent stratification is likely to become established as the upper layers of the lake will become diluted with much less dense Red Sea water, whether or not concentrated in a process of reverse osmosis desalination. When the upper layers will become diluted by more that 10% by the waters
from the Red Sea, combined with any flood waters that naturally enter the Dead Sea each winter, conditions are established for the development of blooms. The extent of these blooms will be a direct function of the availability of phosphate. The waters of the Gulf of Aqaba are very low in phosphate, but other sources (phosphate entering with flood waters from the catchment area, anthropogenic sources) can be quantitatively far more important. The results of simulation experiments documented in this study show that the conditions that lead to the formation of a microbial bloom in the Dead Sea are now quite well understood. They also show that such blooms, once formed, can remain present for long periods and determine to a large extent the properties of the lake for many years.

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References


Legends to the Figures

Figure 1. Numbers of *Dunaliella* cells, concentrations of chlorophyll, numbers of archaeal cells, and concentration of bacterioruberin carotenoids in an outdoor pond filled with a mixture of 80% Dead Sea water and 20% Red Sea water, and amended with 1 µM KH$_2$PO$_4$ from the start of the experiment in March 2003 until August 2005. An additional portion of 1 µM KH$_2$PO$_4$ was added in November 2004 (arrow).

Figure 2. Numbers of *Dunaliella* cells, concentrations of chlorophyll, numbers of archaeal cells, and concentration of bacterioruberin carotenoids in an outdoor pond filled with a mixture of 70% Dead Sea water and 30% Red Sea water. In March 2003 the pond was filled with a 1:1 mixture of water from ponds no. 9 and 10 from an earlier experiment, which contained 70% Dead Sea water – 30% Red Sea and 1 and 10 µM KH$_2$PO$_4$ (Oren et al., 2004), explaining the high initial values of biological parameters.

Figure 3. Development of *Dunaliella* cells and chlorophyll in a laboratory simulation experiment in which Dead Sea – Red Sea water mixtures were incubated for 25 days at 30 °C in the light in the presence of 1 (▲), 2.5 (■) and 5 µM KH$_2$PO$_4$ (●) and an inoculum of 500 *Dunaliella* cells ml$^{-1}$, whereafter the density of *Dunaliella* cells (left panel) and the chlorophyll content of the water (right panel) were determined.

Figure 4. Schematic representation of the processes that govern the development of algal and archaeal blooms in the Dead Sea water column.
Fig. 3

Fig. 4