



THE MINISTRY OF NATIONAL
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GEOLOGICAL SURVEY OF ISRAEL

Geochemical Evolution and Manganese Mobilization in Organic Enriched Water Recharging a Calcareous-Sandstone Aquifer; Clues from the Shafdan Sewage Treatment Plant

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Abstract

The present dissertation focuses on the aquatic geochemistry of Mn during the interaction of groundwater enriched with organic matter with calcareous-sandstone rocks. The site selected for the study was the Yavne-2 infiltration system, which is part of the larger soil aquifer treatment (SAT) system of the Shafdan plant. The processes in the SAT system include rapid infiltration of effluents into a calcareous-sandstone aquifer and their recovery, for reuse in irrigation, after a residence time of a few months within the aquifer.

Due to the high dissolved organic matter load in the effluents, the aquifer reaches redox conditions suitable for Mn reduction and mobilization. About 20 y after the onset of the Shafdan SAT operation, the Mn concentrations in the reclaimed effluents increased from ca. $30 \mu\text{g}\cdot\text{L}^{-1}$ which represent the Mn content in the recharged effluents up to $100\text{--}2200 \mu\text{g}\cdot\text{L}^{-1}$. This increase in Mn concentrations was accompanied by precipitation of Mn oxides in the pipes conveying the reclaimed effluents, resulting in blockages of pipes and other operation problems for the end-users. Thus, the Shafdan is an excellent "natural laboratory" to study Mn geochemistry and mobilization in groundwater. Besides this obvious advantage, the study of this aquifer may provide a method for reducing the Mn oxides precipitation in the Shafdan pipeline that is the major operational problem of the plant.

Accordingly, the overall aim of this study was to identify and quantify the geochemical processes that impact and control the Mn mobilization and the chemical composition of organic rich water as it interacts with the sediments in the vadose zone and within the aquifer. Special attention was given to the processes controlling the Mn retardation within the aquifer and its sudden increase in the reclaimed effluents.

The work carried out during the study included: 1. Collection and synthesis of historical data; 2. Sampling of the recharged effluents in the infiltration basin and along the upper 9 m of the vadose zone, as well as the groundwater pumped from the observation and production wells around the basin; 3. Drilling of five observation wells at the center of the basin and along the groundwater flow path for sampling of water and sediments; 4. Chemical analyses of water and sediment samples; 5. Laboratory adsorption experiments using experimental columns packed with pristine Shafdan sediments; 6. Formulation of a numerical model simulating the Mn retardation in the aquifer; and 7. Quantitative evaluation and synthesis of the data.

Cation exchange and CaCO_3 dissolution were found to be the main processes modifying the chemical composition of the effluents during their flow in the aquifer. This was

deduced from the chemical composition of water collected in wells drilled into the aquifer and from the laboratory simulations.

The pretreated effluents that recharge the aquifer are enriched with organic matter and ammonium, which are oxidized almost completely during the effluent infiltration through the vadose zone. The oxidation of organic matter and the nitrification processes consume the dissolved oxygen (DO), causing suboxic conditions that facilitate reduction of sedimentary Mn-oxide and its mobilization as Mn^{2+} in the groundwater.

The Mn budget for the period from the onset of the Yavne-2 SAT system operation until 2004 indicates clearly that during this period the aquifer rocks lost at least 8 Ton of Mn due to reduction of native Mn-oxides and its mobilization as Mn^{2+} with the groundwater.

The late appearance of the high Mn^{2+} concentrations in the production wells and the location of the front of high Mn^{2+} concentration within the aquifer containing 100% effluents, indicate retardation of the Mn within the aquifer. This Mn retardation is attributed to massive adsorption of reduced Mn(II) onto the aquifer sediments, as simulated also in the experimental columns.

The Mn sorption isotherm obtained from the column experiment simulations, suggests that the total amount of Mn(II) adsorbed onto the Yavne-2 aquifer sediments ranges between 90 and 260 Ton. The experiments also verified that Mn retardation is much greater than that of all major cations during the flow of water through the sandy sediments under suboxic conditions. The Mn^{2+} breakthrough behavior is controlled by the adsorption capacity of Mn(II). Therefore, the higher the Mn^{2+} concentration in the inflow solution, the earlier it appears in the outflow solutions and the sharper is the rise of its breakthrough curve.

Precipitation of MnCO_3 sets the upper limit on Mn^{2+} concentration in the groundwater at high Mn^{2+} concentrations ($>700 \mu\text{g}\cdot\text{L}^{-1}$ for $\text{ALK}=0.005 \text{ eq}\cdot\text{L}^{-1}$ and $\text{pH}=6.8$). A transport-reaction numerical model formulated in the present study suggests that the kinetics of MnCO_3 precipitation is much slower (by at least 3 orders of magnitude) than that of the adsorption, indicating that adsorption is the main process controlling Mn^{2+} retardation.

In summary, a front of high Mn^{2+} concentration advances in the direction of the groundwater flow within the calcareous-sandstone aquifer containing 100% effluents. It is expected that the Mn front will eventually reach the hydrologic trough around the basin, which contains a mixture of effluents and oxidized fresh groundwater. Mixing between these water types will result in oxidation and precipitation of Mn-oxides in the aquifer. Thus, groundwater pumped in wells located within the trough, which at present contains

low levels of Mn, will remain so also in the future. Accordingly, the advance of the Mn front is expected to stop when it reaches the hydrologic trough. The mobilization of Mn in the aquifer is expected to stop when all the labile sedimentary Mn content within the region of the 100% effluents will be consumed. This process is unlikely to happen in the next few decades.

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Abbreviations

ALK	Alkalinity
CEC	Cation Exchange Capacity
DIC	Dissolved Inorganic Carbon
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
LOI	Loss On Ignition
MAC	Mn ²⁺ Adsorption Capacity
MBTP	Mechanical Biological Treatment Plant
MCM	Million Cubic Meters
NKJT	Kjeldahl-nitrogen (organic- <i>N</i> + NH ₄ ⁺)
RE	Recharged Effluents
SAT	Soil Aquifer Treatment
TOC	Total Organic Carbon

Symbols

C	Solute concentration	$\text{mg}\cdot\text{L}^{-1} / \text{meq}\cdot\text{L}^{-1}$
C_0	Initial concentration in column	$\text{meq}\cdot\text{L}^{-1}$
C_{in}	Concentration of inflow solution	$\text{meq}\cdot\text{L}^{-1}$
C_{out}	Concentration of outflow solution	$\text{meq}\cdot\text{L}^{-1}$
s	Adsorbed cation concentration	$\text{mg}\cdot\text{kg}^{-1}$
q	Adsorbed cation concentration	$\text{mg}\cdot\text{L}^{-1}$
K_d	Distribution coefficient	
R	Retardation factor ($K_d + 1$)	
$^{Mn}K_d$	Distribution coefficient of Mn^{2+}	
$^{Mn}K'_d$	'Apparent' distribution coefficient of Mn^{2+}	
ρ_b	Bulk density	$\text{g}\cdot\text{mL}^{-1}$
ε	Porosity	
Z	Aquifer thickness	m
r	Radius from the center of the infiltration basin	m
r_{basin}	Radius of the infiltration basin	m
Q	Annual effluents recharge	$\text{m}^3\cdot\text{y}^{-1}$
v	Flow velocity	$\text{cm}\cdot\text{h}^{-1}$
α	Dispersivity	cm
D	Dispersion coefficient ($\alpha \cdot v$)	$\text{cm}^2\cdot\text{h}^{-1}$
L	Length of an experimental column	cm
A	Cross section area	cm^2
M_{total}	total amount of an exchangeable cation	meq
M_{solid}	total amount of an exchangeable cation on solid	meq
$M_{\text{pore water}}$	total amount of an exchangeable cation in pore water	meq
Δt	Time increment	h

Δx	Distance increment	cm
k_a	Adsorption rate coefficient	h^{-1}
k_p	MnCO_3 precipitation rate coefficient	h^{-1}
ALK	Alkalinity	$\text{eq}\cdot\text{L}^{-1}$
pH	$-\log\{\text{H}^+\}$	
$p\varepsilon$	$-\log\{e^-\}$	
E_{H}	redox potential	volt
$K_{\text{sp, rho}}$	solubility product of MnCO_3	
K_2	Equilibrium constant between HCO_3^- and CO_3^{2-}	
K	Equilibrium constant of a reaction	
Ω	Saturation degree	
PCO_2	Partial pressure of CO_2	ppm
$\{\}$	Activity	
$[\]$	Concentration in $\text{mol}\cdot\text{L}^{-1}$	

Chapter 1

Introduction

Manganese is the third most abundant transition metal in earth's crust ([Morgan, 2000](#)) and the twelfth most abundant element overall ([Maynard, 1983](#)). Manganese enrichment is common in various environments such as sedimentary environments, water reservoirs, and ocean floor. Manganese is an important element for several reasons: 1. Manganese is one of the main components in the steel industry, and due to the worldwide demand for steel products its mining has great economic importance ([Kesler, 1994](#)); 2. Acid mine drainage generally contains high concentrations of manganese, as well as other metals, becoming a source for environmental pollution ([Johnson and Hallberg, 2005](#); [Hallberg and Johnson, 2005](#)); 3. Many trace elements commonly adsorb onto Mn and Fe oxides and hydro-oxides ([Schlieker et al., 2001](#); [Guo et al., 1997](#)). Therefore, dissolution and precipitation of these oxides have a significant impact on the mobilization or retention of trace elements in aquatic and groundwater environments; and 4. Manganese is an essential element in living systems, having some 20 different functions in enzymes and proteins such as in photosystem II and in superoxide dismutase ([Frausto da Silva and Williams, 1991](#)).

Consequently, the geochemistry of manganese and its mobilization is of great interest in many fields of earth sciences, including: ore deposits, oceanic Mn nodules formation, trace element mobilization, biological systems, biogeochemistry of aquatic environments, and water pollution.

The behavior of manganese is governed by oxidation and reduction processes according to the oxidation state of the environment. Generally, the oxidation and reduction processes

and their kinetics are microbially mediated (Myers and Nealson, 1988; Ghiorse, 1989; Lovley, 1991). At low redox potential (E_H) the Mn behavior is dictated by carbonate minerals (Maynard, 1983). The geochemical properties of manganese are similar to those of iron (Maynard, 1983), and due to its depending on the redox conditions, the Mn cycle may be linked to other geochemical cycles of carbon, nitrogen, oxygen, iron, and sulfur (Stumm and Morgan, 1981).

Elevated concentrations of dissolved Mn are widely observed in aquifers recharged by river waters rich in organic matter due to its mobilization in reducing conditions. This type of Mn mobilization has been the focus of several field studies and laboratory experiments (Jacobs et al., 1988; Von Gunten et al., 1991; Matsunaga et al., 1993; Bourg and Bertin, 1993, 1994; Thomas et al., 1994; Ludvigsen et al., 1998; Petrunice et al., 2005). Recharging anthropogenic effluents enriched in organic matter into local aquifers may reach the stage of Mn reduction and mobilization. This recharging becomes common in many populated areas around the world due to the growing demand for water and the need to increase the natural replenishment of groundwater (Asano, 1985).

The system in which effluents are recharged into the local aquifer and are being pumped again for agricultural use is the so called "Soil Aquifer Treatment" (SAT). A SAT system operates at the Shafdan sewage reclamation plant as tertiary treatment of the effluents. This SAT system includes rapid infiltration of pretreated effluents into a calcareous-sandstone aquifer and recovery of the effluents after a residence time of a few months within the aquifer for reuse in irrigation.

Severe degradation in the quality of the reclaimed effluents in the Shafdan SAT system begun ca. 20 y after the onset of operation. The Mn concentrations in the reclaimed effluents increased to 100-2200 ppb from ca. 30 ppb Mn in the recharged effluents. The increase in Mn concentration was accompanied by precipitation of Mn oxides in the pipes conveying the reclaimed effluents resulting in pipeline blockage and operation problems for the end-users.

Due to these phenomena, the Shafdan SAT system was selected for studying the geochemical processes and conditions controlling manganese mobilization in groundwaters. Besides the obvious geochemical advantage of the site, understanding the Mn geochemistry in this aquifer may provide a method for reducing the Mn oxide precipitation in the Shafdan pipeline that is the major operational problem of the plant. The present

study examines the mobilization of Mn by the recharged effluents and describes the geochemical evolution of the water as it interacts with the sediments in the vadose zone and within the aquifer. Particular emphasis was put on the processes dictating the Mn retardation within the aquifer and its sudden increase in the reclaimed effluents. The study was conducted in the SAT system of Yavne - 2 infiltration basin, the basin in which the reclaimed water contains the highest Mn concentrations.

1.1 Geochemical controls on manganese mobilization in groundwater

1.1.1 The sequence of redox reactions in aquatic environments

The most important redox reactions in aquatic environments are the oxidation of organic matter accompanied by reduction reactions of different electron acceptors (Sigg, 2000). The sequence of these reactions (Table 1.1) in the order of decreasing redox potential is presented in Fig. 1.1 Under highly oxidized (aerobic) conditions, bacterial oxidation of organic matter occurs first by reduction of O_2 ($E_H \approx 800$ mV). When the dissolved oxygen (DO) is consumed and the water contains NO_3^- , the next step will be denitrification, which is bacterial reduction of NO_3^- to N_2 gas, until all nitrate is consumed. Further E_H decrease to about 500 mV, may cause organic matter oxidation by MnO_2 . When Mn reduces from (+4) to (+2) it becomes soluble and is readily mobilized as Mn^{2+} . Fe reduction may occur only when $E_H < 0$ mV, followed by sulfate reduction and methane formation under more anaerobic conditions.

As mentioned above, these redox reactions are generally mediated by microbial activity. Therefore, the chemical reaction sequence describes also an ecological sequence of microorganisms, which includes: aerobic heterotrophs, denitrifiers, manganese and iron reducers, sulfate reducers, and methane bacteria (Stumm and Morgan, 1981). The standard free energies (ΔG_w^0) of the sequence of the redox reactions mentioned above, increase in distinct steps (Morel and Hering, 1993 Table 1.1). Despite the stepwise increase in ΔG_w^0 , several of the redox processes (e.g., manganese reduction and denitrification or methane production and sulfate reduction) may occur simultaneously (Ludvigsen et al., 1998).

TABLE 1.1: The redox reaction sequence and the free energies, ΔG_w^0 , released from this microbial mediated reactions. The organic formula "CH₂O" symbolizes 1/6 glucose (Adopted from [Morel and Hering, 1993](#)).

	Reaction	ΔG_w^0 (kJ · mol ⁻¹)
Aerobic respiration	$\frac{1}{4}\text{"CH}_2\text{O"} + \frac{1}{4}\text{O}_{2(g)} \longrightarrow \frac{1}{4}\text{CO}_{2(g)} + \frac{1}{4}\text{CH}_2\text{O}$	-119
Denitrification	$\frac{1}{4}\text{"CH}_2\text{O"} + \frac{1}{5}\text{NO}_{3(aq)}^- + \frac{1}{5}\text{H}^+ \longrightarrow \frac{1}{4}\text{CO}_{2(g)} + \frac{1}{10}\text{N}_{2(g)} + \frac{7}{20}\text{H}_2\text{O}$	-113
Manganese reduction	$\frac{1}{4}\text{"CH}_2\text{O"} + \frac{1}{2}\text{MnO}_{2(s)} + \text{H}^+ \longrightarrow \frac{1}{4}\text{CO}_{2(g)} + \frac{1}{2}\text{Mn}_{(aq)}^{2+} + \frac{3}{4}\text{H}_2\text{O}$	-96.9
Iron reduction	$\frac{1}{4}\text{"CH}_2\text{O"} + \text{Fe}(\text{OH})_{3(s)} + 2\text{H}^+ \longrightarrow \frac{1}{4}\text{CO}_{2(g)} + \text{Fe}_{(aq)}^{2+} + \frac{11}{4}\text{H}_2\text{O}$	-46.7
Sulfate reduction	$\frac{1}{4}\text{"CH}_2\text{O"} + \frac{1}{8}\text{SO}_{4(aq)}^{2-} + \frac{1}{8}\text{H}^+ \longrightarrow \frac{1}{4}\text{CO}_{2(g)} + \frac{1}{8}\text{HS}_{(g)}^- + \frac{1}{4}\text{H}_2\text{O}$	-20.5
Methane formation	$\frac{1}{4}\text{"CH}_2\text{O"} \longrightarrow \frac{1}{8}\text{CO}_{2(g)} + \frac{1}{8}\text{CH}_{4(g)}$	-17.7
Hydrogen fermentation	$\frac{1}{4}\text{"CH}_2\text{O"} + \frac{1}{4}\text{H}_2\text{O} \longrightarrow \frac{1}{4}\text{CO}_{2(g)} + \frac{1}{2}\text{H}_{2(g)}$	-1.1

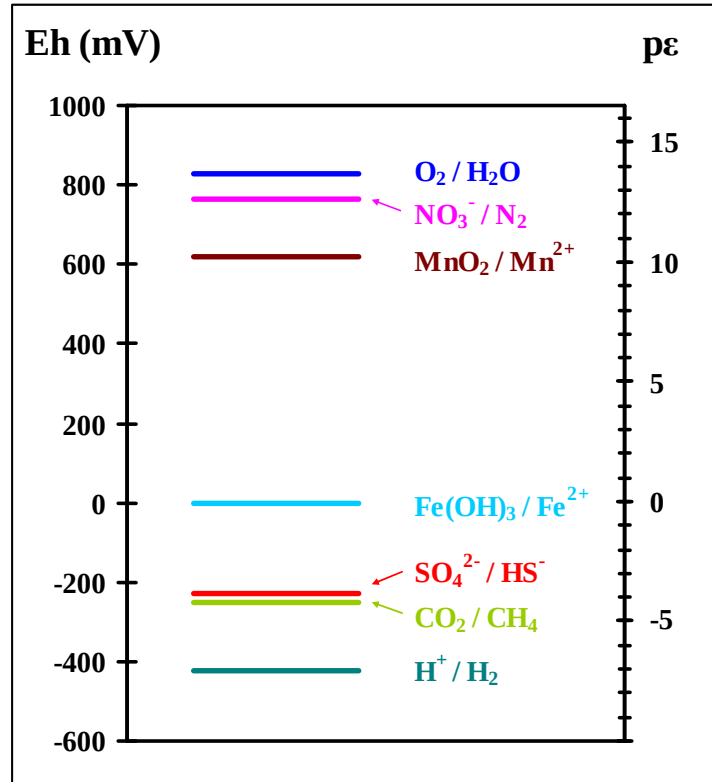


FIGURE 1.1: Redox potential of the most important redox reactions in natural waters at pH=7 and 25°C. The lines represents either the E_H^0 (or pe^0) of each redox pair and were calculated from the standard free energies of the reactions (activities {Red}={Ox}=1). In the case of Mn and Fe, the activities are assumed to be $\{\text{Mn}^{2+}\} = \{\text{Fe}^{2+}\} = 10^{-5}$ mol·L⁻¹. The free energy data were taken from [Garrels and Christ, 1965](#) and from [Stumm and Morgan, 1981](#).

1.1.1.1 Redox zoning

The occurrence of the redox processes described above in a stepwise sequence of reactions causes the formation of distinct zones characterized by presence or absence of indicative redox species such as DO , NO_3^- , Mn^{2+} , Fe^{2+} and SO_4^{2-} (Fig. 1.2; Berner, 1981; Lovley, 1991; Appelo and Postma, 1996). Berner, 1981 divided the sedimentary environments into two major zones according to the DO concentration: *oxic* ($\text{DO} \geq 10^{-6} \text{ mol}\cdot\text{L}^{-1}$) and *anoxic* ($\text{DO} < 10^{-6} \text{ mol}\cdot\text{L}^{-1}$). The anoxic environments were subdivided into a *post-oxic* zone, in which nitrate, manganese and iron are reduced, a *sulfidic* zone, which is characterized by sulfate reduction, and a *methanic* zone, in which methane forms. In many cases not all the zones exist and sometimes some of them are not visible. Aquifers, which are frequently recharged by surface water, remain usually within the *post-oxic* state (Appelo and Postma, 1996).

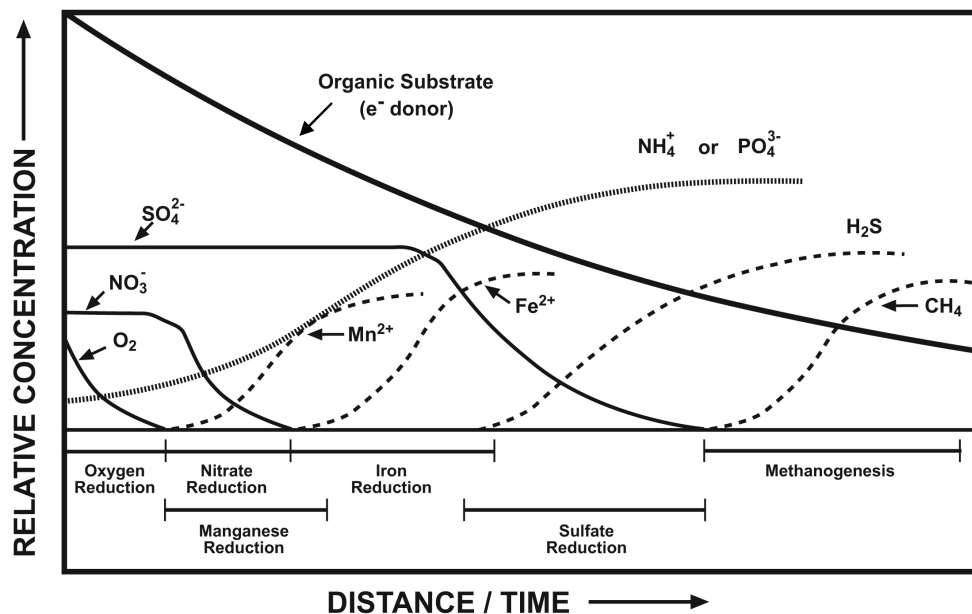


FIGURE 1.2: A schematic presentation of redox zoning that develops along distance or time and characterized by the presence or absence of indicative redox species. From: Lorah, M. M., Cozzarelli, I. M. and Bohlke, J. K., <http://md.water.usgs.gov/posters/nutrientsRedox/index.html>.

In natural environments the redox processes generally proceed sequentially from the highest energy yield downward (Appelo and Postma, 1996). The DO is consumed relatively fast in an aquifer that is recharged with oxygenated water containing a high load of organic matter (Jacobs et al., 1988; Schlieker et al., 2001). In such case the DO concentration decreases dramatically within the upper part of the infiltration flow path.

Then, the next available electron acceptor will be consumed (see the redox sequence in Table 1.1), leading to the development of discrete redox zones along the flow path (Fig. 1.2). This redox zoning may appear in depth profiles of surface or subsurface water bodies, or along a flow path in an aquifer (Lovley and Goodwin, 1988; Chapelle et al., 1995; Appelo and Postma, 1996; Massmann et al., 2008).

A reverse order of reactions occurs when an organic-rich leachate enters an oxic aquifer (Baedeker and Back, 1979; Bjerg et al., 1995; Ludvigsen et al., 1998). Bjerg et al., 1995 described redox zoning in a leachate plume, which included a methanogenic/sulfate reducing zone close to a landfill, followed by iron, manganese, and nitrate reducing zones and an aerobic zone further away from the landfill.

1.1.2 Stability fields of Mn dissolved species and minerals - The $p\varepsilon$ – pH diagram

Manganese behavior is controlled by the redox and acid-base conditions of the environment. The manganese may appear in several oxidation states: +2, +3, +4, +6 and +7. The dominance of the different Mn species is controlled by the "hypothetical" electron and proton activities of a solution. These activities, expressed by the $p\varepsilon$ and pH , respectively, reflect the relative tendencies of a solution to accept or transfer electrons and protons (Stumm and Morgan, 1981). The $p\varepsilon$ is equivalent to the redox potential, E_H , as:

$$p\varepsilon = \frac{F}{2.303 \cdot R \cdot T} \cdot E_H \quad (1.1)$$

where, F - Faraday number ($94,490 \text{ C} \cdot \text{mol}^{-1}$); R - Gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); T - temperature in $^{\circ}\text{K}$.

The $p\varepsilon$ – pH diagram describes the stability fields of various soluble species and solids of an element as calculated from their thermodynamic equilibrium relations. This diagram indicates which species predominate under any given conditions of the solution, $p\varepsilon$ (or E_H) and pH . A $p\varepsilon$ – pH diagram of the $\text{Mn-H}_2\text{O-CO}_2$ system was constructed for the groundwater in the Shafdan SAT system, i.e., Mn concentration of $[\text{Mn}] = 1.8 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ (1000 ppb) and C_T (total carbon) = $6 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (Fig. 1.3). The equations of the lines constructing this diagram are presented in Table 1.2. The equilibrium constants of the reactions (at 25°C), K (Table 1.2), were calculated from the standard

free energy changes for the reactions, ΔG^0 , by the following equation:

$$\log K = \frac{-\Delta G^0}{2.303 \cdot R \cdot T} \quad (1.2)$$

where, R - Gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); T -temperature in °K (298.15 °K). The standard free energy change of a reaction is the sum of the standard free energies of formation, G_f^0 , of the products minus the standard free energies of formation of the reactants ($\Delta G^0 = \Sigma G_f^0_{\text{products}} - \Sigma G_f^0_{\text{reactants}}$).

When the pH of the solution is nearly neutral (about 7), as in the Shafdan aquifer, the Mn may oxidized from its reduced form, as dissolved Mn^{2+} , to more oxidized but the solid phases of MnOOH or MnO_2 at a relatively high pε of about 9 (Fig. 1.3). When precipitated as oxide under high pε, the concentration of Mn in the solution decreases. Under reduced conditions, Mn^{2+} may precipitate as MnCO_3 when the pH increases above 7 (Fig. 1.3), which may occur due to CaCO_3 dissolution. Such precipitation may control the maximum concentration of reduced Mn in an aquifer (Bourg and Bertin, 1994).

It should be noted that in natural environments the waters are in a highly dynamic state with regard to oxidation-reduction rather than being in or near equilibrium (Stumm and Morgan, 1981). Many redox reactions are slow, and therefore the concentrations of oxidized or reduced species may greatly differ from those predicted by the pε–pH diagram. For example, due to slow kinetics, reduced Mn^{2+} may still exist in solution even when DO concentration rises up to $60 \mu\text{mol} \cdot \text{L}^{-1}$ (Bourg and Bertin, 1993), well within the *oxic* state (Berner, 1981).

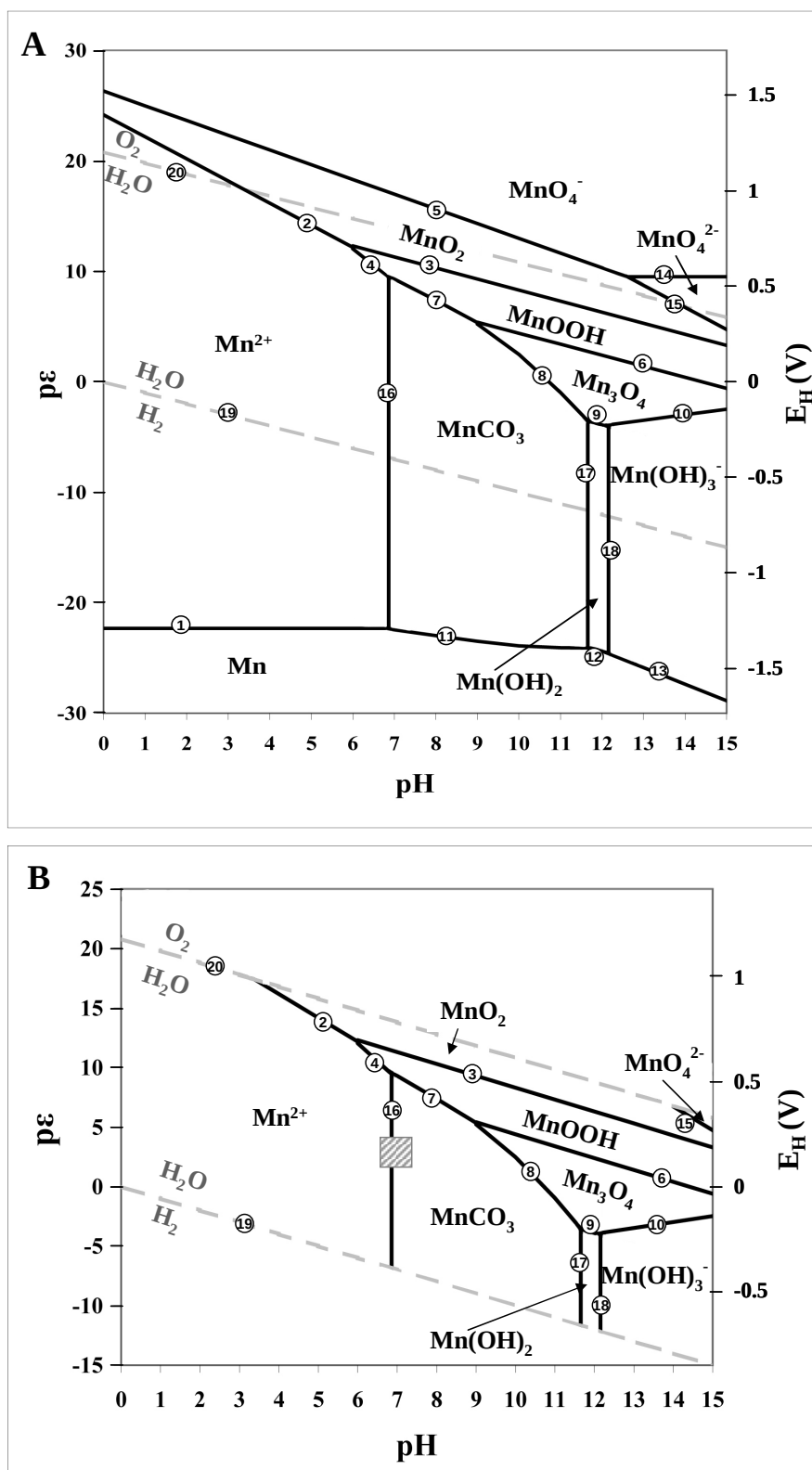


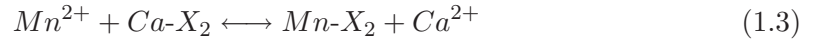
FIGURE 1.3: $p\varepsilon$ - pH diagram for $Mn-H_2O-CO_2$ system ($25^\circ C$), calculated for the Shafdan aquifer concentrations: $[Mn]=1.8 \cdot 10^{-5} \text{ mol} \cdot L^{-1}$, CT (total carbon) $=6 \cdot 10^{-3} \text{ mol} \cdot L^{-1}$. The two diagrams are identical except for the y-axis scale, where in Fig. B only the species fields in the $p\varepsilon$ range of water stability are presented. The grey square in Fig. B represents the conditions prevailing within the Shafdan aquifer. The equations used to construct the diagrams are given in Table 1.2 and their ordinal numbers are also in the diagrams.

TABLE 1.2: Equations for the construction of the pε– pH diagram for the Mn–H₂O–CO₂ system presented in Fig. 1.3. All equations were written in the direction of reduction. The values of log K at 25°C calculated from the standard free energies of formation of the species which are from: ^(a) Garrels and Christ, 1965 and ^(b) Stumm and Morgan, 1981

	Reaction	Log K	Equation
1	$\text{Mn}^{2+} + 2\text{e}^- = \text{Mn}_{(s)}$	-39.9 ^b	$\text{p}\varepsilon = -19.95 + \frac{1}{2} \log\{\text{Mn}^{2+}\}$
2	$\text{MnO}_{2(s)} + 4\text{H}^+ + 2\text{e}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	43.7 ^b	$\text{p}\varepsilon = 21.8 - 2\text{pH} - \frac{1}{2} \log\{\text{Mn}^{2+}\}$
3	$\text{MnO}_{2(s)} + \text{H}^+ + \text{e}^- = \text{MnOOH}_{(s)}$	18.3 ^b	$\text{p}\varepsilon = 18.3 - \text{pH}$
4	$\text{MnOOH}_{(s)} + 3\text{H}^+ + \text{e}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	25.3 ^b	$\text{p}\varepsilon = 25.3 - 3\text{pH} - \log\{\text{Mn}^{2+}\}$
5	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- = \text{MnO}_{2(s)} + 2\text{H}_2\text{O}$	83.8 ^b	$\text{p}\varepsilon = 27.9 - \frac{4}{3}\text{pH} + \frac{1}{3} \log\{\text{MnO}_4^-\}$
6	$3\text{MnOOH}_{(s)} + \text{H}^+ + \text{e}^- = \text{Mn}_3\text{O}_{4(s)} + 2\text{H}_2\text{O}$	14.4 ^b	$\text{p}\varepsilon = 14.4 - \text{pH}$
7	$\text{MnOOH}_{(s)} + \text{HCO}_3^- + 2\text{H}^+ + \text{e}^- = \text{MnCO}_{3(s)} + 2\text{H}_2\text{O}$	25.6 ^b	$\text{p}\varepsilon = 25.6 - 2\text{pH} + \log\{\text{HCO}_3^-\}$
8	$\text{Mn}_3\text{O}_{4(s)} + 3\text{HCO}_3^- + 5\text{H}^+ + 2\text{e}^- = 3\text{MnCO}_{3(s)} + 4\text{H}_2\text{O}$	62.2 ^b	$\text{p}\varepsilon = 31.1 - \frac{5}{2}\text{pH} + \frac{3}{2} \log\{\text{HCO}_3^-\}$
9	$\text{Mn}_3\text{O}_{4(s)} + 2\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^- = 3\text{Mn}(\text{OH})_{2(s)}$	16.2 ^b	$\text{p}\varepsilon = 8.1 - \text{pH}$
10	$\text{Mn}_3\text{O}_{4(s)} + 5\text{H}_2\text{O} + 2\text{e}^- = 3\text{Mn}(\text{OH})_3^- + \text{H}^+$	-34.2 ^a	$\text{p}\varepsilon = -17.1 + \frac{1}{2}\text{pH} - \frac{3}{2} \log\{\text{Mn}(\text{OH})_3^-\}$
11	$\text{MnCO}_{3(s)} + \text{H}^+ + 2\text{e}^- = \text{Mn}_{(s)} + \text{HCO}_3^-$	-40.1 ^b	$\text{p}\varepsilon = -20.1 - \frac{1}{2}\text{pH} - \frac{1}{2} \log\{\text{HCO}_3^-\}$
12	$\text{Mn}(\text{OH})_{2(s)} + 2\text{H}^+ + 2\text{e}^- = \text{Mn}_{(s)} + 2\text{H}_2\text{O}$	-24.8 ^b	$\text{p}\varepsilon = -12.4 - \text{pH}$
13	$\text{Mn}(\text{OH})_3^- + 3\text{H}^+ + 2\text{e}^- = \text{Mn}_{(s)} + 3\text{H}_2\text{O}$	-8.0 ^a	$\text{p}\varepsilon = -4.0 - \frac{3}{2}\text{pH} + \frac{1}{2} \log\{\text{Mn}(\text{OH})_3^-\}$
14	$\text{MnO}_4^- + \text{e}^- = \text{MnO}_4^{2-}$	9.5 ^a	$\text{p}\varepsilon = 9.5 + \log \frac{\{\text{MnO}_4^-\}}{\{\text{MnO}_4^{2-}\}}$
15	$\text{MnO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- = \text{MnO}_{2(s)} + 2\text{H}_2\text{O}$	74.3 ^a	$\text{p}\varepsilon = 37.1 - 2\text{pH} + \frac{1}{2} \log\{\text{MnO}_4^{2-}\}$
16	$\text{MnCO}_{3(s)} + \text{H}^+ = \text{Mn}^{2+} + \text{HCO}_3^-$	-0.21 ^b	$\text{p}\varepsilon = -0.21 - \log\{\text{Mn}^{2+}\} - \log\{\text{HCO}_3^-\}$
17	$\text{Mn}(\text{OH})_{2(s)} + \text{HCO}_3^- + \text{H}^+ = \text{MnCO}_{3(s)} + 2\text{H}_2\text{O}$	15.3 ^b	$\text{p}\varepsilon = 15.3 + \log\{\text{HCO}_3^-\}$
18	$\text{Mn}(\text{OH})_3^- + \text{H}^+ = \text{Mn}(\text{OH})_{2(s)} + \text{H}_2\text{O}$	16.9 ^a	$\text{p}\varepsilon = 16.9 + \log\{\text{Mn}(\text{OH})_3^-\}$
19	$2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_{2(g)} + 2\text{OH}^-$	-28.0 ^b	$\text{p}\varepsilon = -\text{pH} - \frac{1}{2} \log \text{PH}_2$
20	$\text{O}_{2(g)} + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	83.1 ^b	$\text{p}\varepsilon = 20.8 - \text{pH} + \frac{1}{4} \log \text{PO}_2$

1.1.3 Manganese adsorption

Adsorption is the most important process responsible for the retardation (or even elimination) of pollutant chemicals in aquifers and soils (Appelo and Postma, 1996). Metal ions are highly adsorbed on surfaces of clay minerals, organic matter, and oxides/hydroxides. At trace levels they may adsorb onto the sediments through different mechanisms such as electrostatic adsorption, surface complexation and cation exchange (Appelo and Postma, 1996). When a metal, M, adsorbed on an exchange site, X, is denoted by $M-X_i$, where i is the valence of M. The exchange of Mn^{2+} for Ca^{2+} , for example, is:



The equilibrium constant of this reaction, $K_{Mn/Ca}$, which is called the "exchange coefficient" or the "selectivity coefficient", is the relative tendency of the two elements to be adsorbed onto the soil solids (Stumm, 1992; Appelo and Postma, 1996). When the Mn (or any other element) is present in solution in trace concentration, a change in its concentration will change its adsorbed concentration but will not change the exchangeable fraction of the major cations (Appelo and Postma, 1996). The ratio between the adsorbed and the solute concentrations of the trace element (e.g. Mn) is expressed by its distribution coefficient, $^{Mn}K_d$:

$$^{Mn}K_d = \frac{[Mn-X_2]}{[Mn^{2+}]} \quad (1.4)$$

Adsorption of metals is strongly dependent on the pH; the higher the pH is, the higher the adsorption (Flogeac et al., 2005). This dependence results from the extremely high affinity of protons to the exchange sites on the solids. Mn adsorption is characterized by (Flogeac et al., 2005): 1. great affinity to soils; 2. the Mn sorption isotherm is not linear (like $^{Mn}K_d$) but rather convex; 3. Mn begins to be adsorbed at pH=6 with maximum adsorption at pH of ca. 8; and 4. the manganese adsorption is a relatively rapid process - in batch experiments the adsorption reached equilibrium within 10 h.

1.1.4 Kinetics of relevant manganese reactions

The kinetics of Mn oxidation and reduction, Mn adsorption and rhodochrosite precipitation are described below.

Mn oxidation: The kinetics of Mn(II) oxidation to Mn(III) and Mn(IV) by dissolved oxygen is dependent upon the pathways available in a specific aquatic environment, e.g., abiotic homogeneous solution oxidation, oxide surface catalysis, or bacterial oxidation (Morgan, 2005). The Mn(II) half-lives at pH=8 for these pathways are: 10 hours, 30 days and 400 days for bacterial oxidation, oxide surface catalysis and homogeneous solution oxidation, respectively (Morgan, 2005).

The rate constant of abiotic oxidation of Mn(II) depends on O_2 concentration, pH, temperature, speciation of Mn(II) in solution, and the nature of the MnO_x surface formed in the reaction (Morgan, 2000). Oxidation of manganese in the absence of a precipitate or solid surface proceeds very slowly (Morgan, 2000). The pseudo first order rate constant for homogeneous Mn(II) oxidation increases linearly with pH (Morgan, 2000, 2005). At 25°C the homogeneous Mn(II) oxidation rate constants range between $8.4 \cdot 10^{-5} \text{ h}^{-1}$ at pH=8.03 (Von Langen et al., 1997) and $3.4 \cdot 10^{-2} \text{ h}^{-1}$ at pH=9.25 (Davies and Morgan, 1989).

Metal oxide surfaces accelerate the rate of Mn(II) oxidation by O_2 . In this process Mn is first adsorbed and then oxidizes (Hem, 1981; Morgan, 2005). This enhancement was observed for surfaces of hematite, manganese dioxide (Wilson, 1980), goethite and lepidocrocite (Davies and Morgan, 1989). The rate of this surface catalyzed reaction may be inhibited by other metal ions competing with Mn(II) for the adsorption sites. Ligands, which can lower the free Mn(II) ions in solution and thus decrease adsorption, may also inhibit surface catalyzed reactions (Morgan, 2005). For pH=8, $PO_2=0.21 \text{ atm}$, and $1 \text{ mg} \cdot \text{L}^{-1}$ of metal oxide particles, Morgan, 2005 obtained a first order rate constant of Mn(II) oxidation of 10^{-3} h^{-1} .

Mn(II) is oxidized by a wide variety of bacteria (Morgan, 2005). Microbial oxidation of Mn(II) is faster by up to 5 orders of magnitude than abiotic Mn(II) oxidation (Tebo,

1991). The kinetics of the bacterial oxidation depends on the characteristics of the bacterial species and their biomass concentrations. Generally, it is described by a "Michaelis-Menten"-like saturation equation (Morgan, 2000):

$$V_0 = \frac{V_{max} \cdot [Mn(II)]}{K_m + [Mn(II)]} \quad (1.5)$$

where, V_0 - initial rate; V_{max} - maximum rate; and K_m - "Michaelis constant". At $[Mn(II)] = K_m$, $V_0 = 1/2 \cdot V_{max}$. Reported V_{max} values ranged between $4 \cdot 10^{-4} \text{ nM} \cdot \text{h}^{-1}$ in the Sargasso Sea (Sunda and Huntsman, 1988) and $67 \text{ nM} \cdot \text{h}^{-1}$ in the Black Sea, nearshore (Tebo, 1991). In general, the rate of bacterial Mn oxidation, as well as Mn reduction, is accelerated by sunlight. It was suggested however that bacterial oxidation of Mn is photoinhibited by high light intensity in surface waters (Sunda and Huntsman, 1988, 1990). A first order rate constant of bacterial oxidation of Mn(II) in natural fresh waters was calculated (for pH=8, $PO_2=0.21 \text{ atm}$, 25°C) to be $4 \cdot 10^{-2} \text{ h}^{-1}$, compared to ~ 10 to 10^{-1} h^{-1} in sea water (Morgan, 2005).

Mn Reduction: Reduction of Mn oxides by organic compounds and different inorganic reductants, such as sulfide, Fe(II), arsenite, and Cr(III) are energetically favorable under most natural water conditions (Morgan, 2000). Therefore, the rate of Mn reduction is much faster than Mn oxidation. The rate of Mn oxide reduction depends on the process that takes place, which, like in the case of oxidation, may be chemical, photochemical or bacterial. The rate of chemical reduction of Mn(III, IV) oxides may vary by 4 orders of magnitude, depending on the different substrates that reduced the oxides (Stone and Morgan, 1984). Apparent second-order rate constants for different simple low molecular weight organic compounds in neutral pH, ranged from $5 \cdot 10^{-3}$ to $20 \text{ M}^{-1} \cdot \text{s}^{-1}$ (Stone and Morgan, 1984). Photoreductive dissolution of MnO_x particles was measured by Waite and Szymczak, 1993 in eastern Caribbean surface waters. They estimated production rates of dissolved Mn from ~ 20 to $1300 \text{ pM} \cdot \text{h}^{-1}$ at 365 nm wavelength irradiation. Bacterial respiration may utilize a MnO_2 solid as the terminal electron acceptor, and thereby release Mn(II) to solution (Myers and Nealson, 1988; Lovley and Phillips, 1988; Lovley, 1991). The rates of MnO_2 reduction by the bacterium MR-1 in a lake-water medium, with acetate or succinate as the carbon source, were observed to be proportional to cell numbers, ranging from $\sim 1 \cdot 10^{-9}$ to $\sim 10 \cdot 10^{-9} \mu\text{mol} \cdot \text{cell}^{-1} \cdot \text{h}^{-1}$ (Myers and Nealson, 1988). The maximum rate of microbial reduction of Mn in a leachate plume was estimated to be $2.4 \text{ nmol Mn(II)} \cdot (\text{g dry sediment})^{-1} \cdot \text{day}^{-1}$ (Ludvigsen et al., 1998).

Mn adsorption: Metal adsorption is considered a rapid reaction with equilibration times on the order of minutes to hours and usually observed to be reversible on the same time scale (Morel and Hering, 1993). Most metal ions have adsorption rates to oxide minerals higher than $10^{0.5} \text{ M}^{-1} \cdot \text{s}^{-1}$ (Stumm, 1992). Hachiya et al., 1984 reported Mn^{2+} adsorption and desorption rate constants of $(3.2 \pm 0.5) \cdot 10^1$ and $(1.8 \pm 0.3) \cdot 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$, respectively, on a $\gamma\text{-Al}_2\text{O}_3$ surface at 25°C . They found that the order of the adsorption rate constants of metal ions corresponded to that of the rate constants for the release of a water molecule from hydrated metal ions in homogeneous metal complex systems. These authors also observed double relaxations of the divalent metal ions onto the aqueous $\gamma\text{-Al}_2\text{O}_3$ suspensions; both the fast and slow relaxation times decrease with the concentration of the metal ions and increase with that of protons.

MnCO_3 precipitation: Many precipitation-dissolution reactions that occur in aquatic systems are slow compared to the residence time of water (Morel and Hering, 1993). Therefore, frequently the chemical composition of water in natural systems does not reach thermodynamic equilibrium with respect to mineral dissolution/precipitation, but rather stabilizes on a steady state composition according to the balance between the water flow velocity and the reaction kinetics.

Precipitation or dissolution is determined by the saturation degree, Ω , of a solution with respect to the relevant mineral. Precipitation takes place when the solution is in oversaturation, $\Omega > 1$. The higher the oversaturation is, the higher is the precipitation rate. The rate of precipitation is often calculated by the empirical expression (Morel and Hering, 1993):

$$r_p = k_p \cdot (\Omega - 1)^n \quad (1.6)$$

where, r_p - precipitation rate and k_p - precipitation rate coefficient.

Rhodochrosite precipitation is a slow process. Rate constants of this process were estimated by model simulations of column experiments to be in the range of $6 \cdot 10^{-13} - 3 \cdot 10^{-12} \text{ mol} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ (Matsunaga et al., 1993).

1.1.5 Aquifer characteristics and the mobilization of Mn

Besides thermodynamics and kinetics, the biogeochemical interactions of Mn and in particular its mobilization may be controlled by physical and chemical characteristics

of the aquifer. Such characteristics include: the chemical composition of the sediments and groundwater, the aquifer mineralogy and texture, the hydraulic conductivity along the aquifer, and the types of the existing organic matter (Hiscock and Grischek, 2002).

Clay layers can enhance reduction and dissolution of Mn (Bourg and Bertin, 1994). Clay causes a decrease in the groundwater flow rate, which leads to faster depletion of oxygen. Within clay layers, which may be enriched in organic matter, the diffusion of the dissolved electron acceptors may be limited by the texture of the sediments, and thus micro niches with extremely anaerobic conditions may develop (Ludvigsen et al., 1998). In addition, the adsorption capacity of these clay layers is extremely high, which may also affect the Mn mobilization within the aquifer by increasing its retardation.

The type of the metal oxides within the aquifer rocks controls the microbial reduction of Mn, e.g., Mn reduction on amorphous metal oxide phases is faster than on crystalline phases (Burdige et al., 1992; Bourg and Bertin, 1994).

The temperature of the recharged water as well as the temperature within the aquifer may also impact Mn mobilization. Seasonal variations in concentration of dissolved Mn in several aquifers (high concentrations in summer and lower in winter) have been explained by seasonal fluctuations in biological activity and/or mineral solubility due to seasonal fluctuations in temperature (Jacobs et al., 1988; Von Gunten et al., 1991; Bourg and Bertin, 1994). Bourg and Bertin, 1994 suggested a threshold temperature of 10°C to trigger and maintain microbial-mediated Mn reduction.

1.1.6 Environments of Mn mobilization

Mobilization of Mn is common in aquatic environments characterized by high organic matter load, suboxic or anaerobic conditions, low-neutral pH, and a Mn source which is usually natural Mn oxides. A few examples for such environments are described below.

High concentrations of Mn are common in aquifers that are recharged by river waters, known as "river-bank filtration systems", which contain a high organic matter load (Jacobs et al., 1988; Von Gunten et al., 1991; Bourg and Bertin, 1993, 1994; Thomas et al., 1994; Schlieker et al., 2001; Petrunice et al., 2005). The elevated Mn concentrations have been attributed to reductive dissolution of sedimentary Mn oxides due to microbial oxidation of the organic matter under suboxic conditions. In these aquifers,

seasonal variations in the Mn concentrations were observed and attributed to temperature changes (Jacobs et al., 1988; Von Gunten et al., 1991; Bourg and Bertin, 1994). An aquifer zone within 20 m from a river bank was found to be slightly reduced, depleted in O_2 , DOC, NO_3^- , Na^+ and K^+ and enriched in Mn^{2+} , Ca^{2+} , Mg^{2+} , HCO_3^- and silica (Bourg and Bertin, 1993). These geochemical trends were attributed to bacterial degradation of organic matter, weathering of Ca and Mg carbonates and quartz minerals and cation exchange between the monovalent and the divalent cations (Bourg and Bertin, 1993).

A high concentration Mn front showed retardation between two wells located along the flow path of a 'river-bank filtration' aquifer (Thomas et al., 1994). This retardation was attributed to three processes: 1. the time required to build up the size of the microbial population capable to oxidize organic matter with Mn oxides; 2. the time required to replace the original groundwater by the infiltrated river water; and 3. the time required for the infiltrated river water to equilibrate with the aquifer sediments with respect to Mn(II) (Thomas et al., 1994).

Migration of municipal landfill leachates enriched in dissolved organic matter show a sequence of anaerobic microbial reduction processes within the pollution plume (Christensen et al., 1994; Bjerg et al., 1995; Ludvigsen et al., 1998). In this case, where extremely anaerobic leachate enters an aerobic aquifer, the leachate plume indicates methanogenesis, sulfate reduction and iron reduction in the first part of the flow path, close to the landfill, followed by manganese reduction and nitrate reduction further downstream (Ludvigsen et al., 1998).

In stratified marine and lake environments, manganese plays an important role as both an electron acceptor and an electron donor in redox processes (Neretin et al., 2003). Dissolved Mn^{2+} concentration increases below the thermocline or halocline, where anoxic conditions develop periodically in the bottom waters (Tercier-Waeber et al., 1998; Neretin et al., 2003). The dissolved Mn^{2+} and the particulate MnO_x profiles in the Baltic Sea (Gotland Deep basin) are characterized by: 1. low concentrations in the upper oxic part of the water column; 2. maximum of particulate MnO_x concentration accompanied by dissolved Mn^{2+} disappears at depths between 70 and 120 m, changes temporally both location and magnitude; and 3. increases in the dissolved Mn^{2+} concentrations below depths of 90-130 m (Neretin et al., 2003). The particulate Mn formation in the oxic

zone is explained by different mechanisms, including microbial Mn oxidation, chemical sorption on suspended particles, and uptake by algae. The elevated concentrations of dissolved Mn^{2+} in the lower anoxic zone were attributed to two sources of Mn^{2+} : 1. reductive dissolution of sinking MnO_x particles; and 2. benthic flux of sedimentary Mn^{2+} (Neretin et al., 2003).

Similar Mn profiles were observed in two lakes in Switzerland (Tercier-Waeber et al., 1998). In Lake Bret and Lake Lugano, low concentrations of dissolved Mn were measured in the oxic surface water and high concentrations up to $7 \mu\text{mol}\cdot\text{L}^{-1}$ were measured in the deep water below 12 m and 90 m depth, respectively, where the conditions are anoxic or suboxic. These profiles indicate oxidative loss of Mn(II) in the surface oxygenated water, and reductive dissolution of MnO_x in the anoxic water and sediments, which dominates the deep water (Tercier-Waeber et al., 1998).

High Mn concentrations are also common in acid mine drainage from coal and metal mines (Hallberg and Johnson, 2005; Johnson and Hallberg, 2005). The acid conditions in these mines prevent the oxidation of Mn^{2+} to solid Mn oxides, leaving high Mn^{2+} concentrations in solution. For this reason, accelerating the removal of Mn(II) by catalyzing the oxidation and precipitation of Mn from the water was a subject of substantial research efforts. These include development of specific fixed bed aerated bioreactors (Hallberg and Johnson, 2005) and subsurface flow wetland with limestone gravel (Hedin et al., 1994; Sikora et al., 2000).

The world's largest Mn deposits are the Mn-oxide nodules common in the abyssal plains of the world ocean (Murray and Renard, 1891; Mero, 1965). The nodules usually appear at the water-sediment interface, or lying on top of the sediments (Maynard, 1983). Whether the origin of this Mn is from submarine volcanism and/or transported from continental weathering is controversial (Arrhenius et al., 1964). In any case, the rate of the Mn oxidation on the ocean floor is controlled by the advection of the dissolved oxygen (Arrhenius et al., 1964).

1.2 Geochemical processes that impact groundwater composition in a calcareous-sandstone aquifer

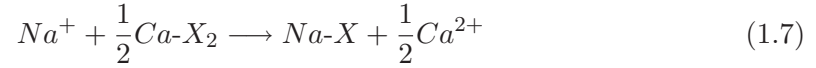
Recharge of aquifers by alien water, such as sea water, irrigation water or effluents, results in intensive geochemical processes that alter the groundwater composition (Appelo and Willemssen, 1987; Appelo et al., 1990; Vengosh and Keren, 1996; Panagopoulos et al., 2004; Greskowiak et al., 2005; Andersen et al., 2005; Lambrakis, 2006; Pavelic et al., 2007). Salinization of coastal aquifers, either by seawater intrusion or by infiltration of polluted water, which has become an important issue, is usually accompanied by cation exchange and by mineral precipitation and dissolution reactions (Chapelle and Knobel, 1983; Magaritz and Luzier, 1985; Appelo and Willemssen, 1987; Pulido-Leboeuf, 2004; Sivan et al., 2005; Kass et al., 2005; Lambrakis, 2006). Infiltration of water enriched in fertilizers or organic matter causes an increase in the nitrate loads in the groundwater (Gormly and Spalding, 1979; Kaplan and Magaritz, 1986; Wassenaar, 1995; Bohlke and Denver, 1995; Hudak, 2000; Oren et al., 2004; Panagopoulos et al., 2004). The main geochemical processes that may affect the groundwater composition within a calcareous-sandstone aquifer such as exists in the Shafdan plant area are briefly outlined below.

1.2.1 Cation exchange

Soils and aquifers contain abundant materials, mainly clay minerals, organic matter and oxides-hydroxides, which are able to adsorb dissolved chemicals from the water (Appelo and Postma, 1996). The sorption is part of the cation exchange reaction whereby a cation is replaced by another on the solid surface. Quantitatively, this process is limited by the cation exchange capacity (CEC) of the sediments, which is the capacity of sediment to adsorb positively charged ions, expressed usually in units of $\text{meq} \cdot (100 \text{ g dry sediment})^{-1}$. The CEC is a function of the specific surface of the sediment and therefore increases with increasing clay and organic matter contents (Appelo and Postma, 1996).

In general, fresh groundwater in carbonatic coastal aquifers contains mostly Ca^{2+} and HCO_3^- whereas seawater contains mostly Na^+ and Cl^- . Therefore the dominant exchange process during seawater intrusion is between Ca^{2+} and Na^+ , whereby the Na^+ is adsorbed onto the sediments and the Ca^{2+} is released into the water (Magaritz and Luzier, 1985; Appelo and Willemssen, 1987; Appelo and Postma, 1996; Sivan et al., 2005).

Following Eq. 1.3:



As a result, seawater within the aquifer becomes enriched in Ca^{2+} and depleted in Na^+ compared to the original seawater. A similar exchange reaction dominates the aquifer when irrigation water or effluents recharges a freshwater aquifer (Vengosh and Keren, 1996; Stigter et al., 1998; Panagopoulos et al., 2004; Kass et al., 2005). The reverse process takes place during aquifer "refreshening", i.e., when fresh water flushes out salt water from an aquifer (Appelo, 1994; Appelo and Postma, 1996).

The affinity of different cations to most sediments follows the lyotropic series, which is determined by the ionic charge and size of the cations (Stumm, 1992; Appelo and Postma, 1996); the higher the cation charge is the greater is its affinity, while the affinity of cations with similar charge increases with increasing non-hydrated radius (i.e. decreasing hydration number). Thus, the order of the affinity of the major cations is: $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ (Chapelle and Knobel, 1983).

Cations that have strong affinity to the solid exchanger will displace other cations and be transported at a relatively low velocity compared to other cations (Appelo and Postma, 1996). As a result, the exchangeable cations will appear in the solution flowing through the sediments in an ordered manner, the first of which will be the cation with least affinity etc., thereby defining a chromatographic behavior.

The cation distribution in the exchange sites, i.e. the cation fractions out of the CEC, depends on the water composition and the exchange coefficients between the cations (see section 1.1.3). Accordingly, the cation fractions may be calculated based on these parameters, as described in detail in Chapter 6.

1.2.2 The carbonate system

The main sources of carbon in water are weathering minerals, atmospheric CO_2 and decomposing organic matter (Stumm and Morgan, 1981). The following description refers to a closed system, which cannot exchange CO_2 with the atmosphere.

The total dissolved inorganic carbon (DIC) includes four species:

$$DIC = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (1.8)$$

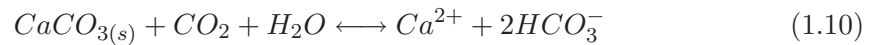
The concentrations of DIC and the different species are given in $\text{mol}\cdot\text{L}^{-1}$. The concentrations of carbon dioxide and carbonic acid, which have a constant ratio between them, are usually expressed together as $H_2CO_3^*$. The concentration ratios between the species depend on the pH of the solution: at low pH values (<6.3 in fresh water) the predominant species is $H_2CO_3^*$; at high pH values (>10.3 in fresh water) the predominant species is CO_3^{2-} ; and at the intermediate values the predominant species is HCO_3^- (Stumm and Morgan, 1981; Appelo and Postma, 1996).

Alkalinity is an important constituent in the interpretation of the carbonate system. Water alkalinity, expressed in $\text{eq}\cdot\text{L}^{-1}$, is the sum of equivalents of the bases that are titratable with a strong acid (Stumm and Morgan, 1981). It is often determined by titration with an HCl solution of known normality towards a pH endpoint of ca. 4.5 (Appelo and Postma, 1996). In practice, most of the alkalinity and often all of it is derived from the carbonate system and may be expressed as:

$$ALK = [HCO_3^-] + 2 \cdot [CO_3^{2-}] + [OH^-] - [H^+] \quad (1.9)$$

Other species that may contribute to the alkalinity include weak acids such as borates, dissolved silicates, ammonia, organic bases, sulfides, and phosphates. However, the concentrations of these non-carbonate components are usually very small in comparison to the carbonate species (Stumm and Morgan, 1981).

Water may lose or gain dissolved carbon during its flow in an aquifer through precipitation or dissolution of carbonate minerals such as calcite (CaCO_3):



The precipitation and dissolution of CaCO_3 are influenced by, but also have an effect on the pH of the water, thereby acting as a buffer in natural waters. Respiration or oxidation of organic matter is a major source of CO_2 in soils and aquifers (Appelo and

[Postma, 1996](#)). This process may be expressed by the general equation:



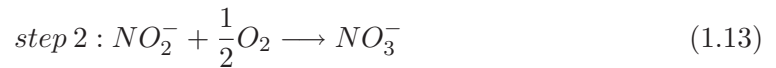
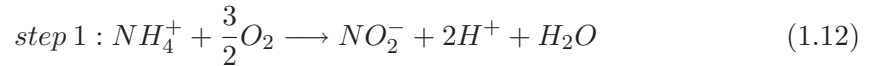
Depending on water pH, the product CO_2 may produce carbonic acid which reacts with the alkaline minerals. Therefore, $CaCO_3$ dissolution is enhanced when the water or the sediments are rich in organic matter that oxidizes and creates this acid.

Dissolution or precipitation of $CaCO_3$ (Eq. 1.10) increases or decreases both the DIC and alkalinity with a ratio of 1:2, while addition or removal of CO_2 (Eq. 1.11) increases or decreases the DIC without changing the alkalinity.

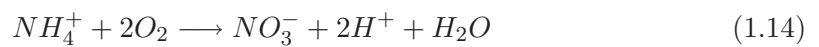
1.2.3 The nitrogen system

Nitrogen usually appears in oxic groundwater in its most oxidized form i.e. nitrate, NO_3^- . The major sources of high nitrate concentrations in groundwater are: 1. enhanced mineralization of organic nitrogen due to intensive cultivation of agricultural fields; 2. application of fertilizers and manure in agricultural fields; and 3. concentrated animal waste or human sewage ([Heaton, 1986](#)). Nitrate is a highly soluble ion and the attenuation of its concentration in groundwater is limited to dilution or denitrification ([Clark and Fritz, 1997](#)).

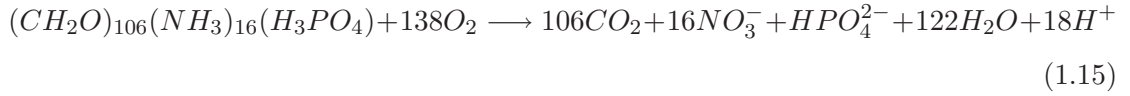
Nitrogen is a dominant constituent in wastewater, and is present mostly in its reduced forms, NH_4^+ and organic-N. Under aerobic conditions NH_4^+ is oxidized to NO_3^- by a two-step process called **nitrification** ([Morel and Hering, 1993](#); [Clark and Fritz, 1997](#)):



where the overall reaction is:

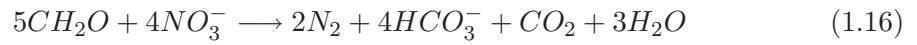


In addition, NO_3^- concentration may increase due to mineralization of organic matter, as represented by the Redfield equation ([Bourg and Bertin, 1993](#)):



Both, nitrification and organic matter mineralization consume oxygen and produce acidity.

Denitrification, reduction of NO_3^- to N_2 , occurs under suboxic or anaerobic conditions. Commonly, denitrification occurs through oxidation of organic matter ([Appelo and Postma, 1996](#)):



This process involves intermediate species such as NO_2^- , NO , N_2O , which are sometimes found in groundwater in low concentrations. Oxidation of reduced solids and other dissolved components such as pyrite, Fe(II)-silicates, Fe^{2+} , H_2S and CH_4 may also be involved in the denitrification process ([Appelo and Postma, 1996](#)). All these oxidation and reduction processes are microbially mediated ([Morel and Hering, 1993](#); [Clark and Fritz, 1997](#)).

To conclude, NO_3^- concentration in groundwater depends on several factors, including anthropogenic inputs and nitrification processes, which act to increase these concentrations, and denitrification which removes nitrate from the water ([Jacobs et al., 1988](#)).

1.3 Artificial recharge of effluents

Artificial recharge of groundwater is becoming increasingly important in water management due to the growing demand for water and the need to increase groundwater replenishment. The purposes of artificial recharge are ([Asano, 1985](#)): 1. reduce, stop, or even reverse declining groundwater levels ; 2. protect freshwater in coastal aquifers against seawater intrusion; 3. utilize the aquifer as an underground reservoir to store surface water, including floods and reclaimed wastewater, for future use; and 4. improve the quality of reclaimed wastewater by soil aquifer treatment (SAT).

1.3.1 Soil Aquifer Treatment (SAT) systems

Soil aquifer treatment (SAT) is considered an efficient tertiary treatment in wastewater reclamation process. The SAT systems include rapid infiltration of pretreated (secondary) effluents to an aquifer and their recovery after a defined residence time. This technique utilizes the vadose zone and the aquifer as a physical, chemical and biological filter to remove essentially all biodegradable organics, suspended solids, bacteria and viruses from the wastewater, and almost all the phosphorus and heavy metals (Bouwer, 1985).

The advantages of the SAT system include large throughput volumes of effluents, use of the recharging aquifer as an underground reservoir, high quality of the reclaimed effluents, simplicity of operation, low operational costs, and the reliability of the system (Idelovitch and Michail, 1984; Bouwer, 1985).

Generally, the effluents are introduced to the aquifer through infiltration basins which are intermittently flooded and allowed to dry. The drying is necessary to allow suspended solids, mainly organic matter that accumulates on the bottom of the basins, to dry and partially decompose. This restores the infiltration rates that tend to decrease during flooding, while at the same time allows air to penetrate the soil to decompose organic material and nitrify ammonium (Bouwer, 1985).

To recycle as much of the wastewater as possible, the infiltration rate should be much higher than that of evapotranspiration. Therefore, the sediments on the surface of the infiltration basins and below should be permeable enough to accommodate high hydraulic loads, but fine enough to provide adequate treatment of the wastewater as it flows through them. The best soils for this purpose should contain a few percents of clay within a texture range of sandy loam, loamy sand and fine sand (Bouwer, 1985). Accordingly, the Israeli coastal plain aquifer is particularly suited to be used for SAT. After their infiltration to the ground, the effluents flow down through the vadose zone and reach the aquifer. Here they displace the native groundwater and move mostly horizontally through the aquifer, away from the infiltration basin (Bouwer, 1985). The renovated effluents are generally recovered by a series of wells surrounding the infiltration basin, thereby defining the aquifer volume that is dedicated to the SAT and renovation of the wastewater.

1.3.1.1 Geochemical processes in SAT systems

A range of geochemical processes and water-rock interactions are responsible for the improvement in the quality of the effluents and changes in their composition during the flow through the vadose zone and within the aquifer in SAT systems (Idelovitch and Michail, 1984, 1985; Bouwer, 1985; Andelman, 1994; Vengosh and Keren, 1996; Idelovitch et al., 2003). The main processes are described below.

Organic compounds: organic compounds are exceptionally variable in their mobility, volatility and persistence in soil. The volatile compounds volatilize prior to entrance to the soil. The particulate organic compounds are removed from the effluents by filtration through the upper soil layer and/or biodegradation in the soil. The dissolved organics enter the soil and are removed by two processes which complement one another: biodegradation and adsorption; part of the organic matter adsorbed onto soil particles undergoes biological degradation over time (Idelovitch et al., 2003). Most of the organic compounds are removed from the effluents within the upper part of the vadose zone (Andelman, 1994; Vengosh and Keren, 1996).

Nitrogen: Nitrogen is a common constituent in wastewater and is mainly present in the form of NH_4^+ and organic- N. In the soil, most of the NH_4^+ is biologically nitrified to NO_3^- , which is a mobile anion. The processes that may remove nitrogen from the effluents in the SAT system include: 1. coarse filtration of particles containing organic-N in the uppermost sediments; 2. denitrification of the NO_3^- to nitrogen (N_2) and nitrous gases (N_2O , NO_x), which escape to the atmosphere, under anaerobic conditions; 3. NH_4^+ adsorption to clay minerals; and 4. volatilization of ammonia.

Phosphorus: Phosphorus is removed from the recharged effluents through fast sorption and/or slow precipitation reactions to amorphous or crystalline forms. At low pH the phosphates precipitate with iron and aluminum, whereas under alkaline conditions the phosphates precipitate with calcium (Andelman, 1994).

Trace metals: Trace metals present in suspended matter are removed from the recharged effluents mainly by mechanical surface filtration and by adsorption onto the surface of the stationary soil matrix (Chang and Page, 1985). Dissolved trace metals may adsorb during cation exchange to clay mineral surfaces, adsorb to amorphous and crystalline

forms of iron, manganese and aluminum oxides, and precipitate to metal hydroxides and carbonates.

Pathogens: Large pathogens, including parasitic protozoa and helminthes and bacteria, are removed effectively by filtration. Bacteria may also be removed by adsorption. Viruses are thought to be removed in the SAT only by adsorption to solid material (Gerba and Goyal, 1985). The survival and retention of the pathogens in the subsurface are largely determined by three factors: the climate, the nature of the soil and the nature of the microorganism (Gerba and Goyal, 1985).

1.4 The Shafdan Plant

The Shafdan sewage reclamation plant accommodates much of the municipal wastewater of the Tel Aviv metropolitan area, which is the most populated region in Israel. The plant is located in the sand dunes above the coastal plain aquifer of Israel, south of metropolitan Tel Aviv and 3-5 km inland from the Mediterranean Sea coastline (Fig. 1.4). The wastewater is treated in a modern mechanical-biological treatment plant (MBTP) and is subsequently recharged to the aquifer for tertiary treatment in the soil and the aquifer (SAT). After a residence time of a few months and up to one year, the effluents are reclaimed by a series of production wells (Fig. 1.4). The reclaimed water is then supplied for unrestricted irrigation to the Negev through a dedicated pipeline (the "third line").

The facility, which has been in operation since 1977, has treated and recharged about $2000 \cdot 10^6 \cdot \text{m}^3$ (2000 MCM) of effluents and presently reclaims some 110 – 130 MCM of effluents annually. The wastewater before and after each treatment in the facility and along the SAT system is sampled and analyzed frequently and all data is summarized in annual reports of Mekorot Water Co. (Michail et al., 1988, 1989, 1990, 1991; Kanarek et al., 1992, 1993, 1994, 1995; Soffer et al., 1996, 1997; Kanarek et al., 1998; Icekson-Tal et al., 1999, 2000, 2001, 2002, 2003b, 2004, 2005, 2006, 2007).

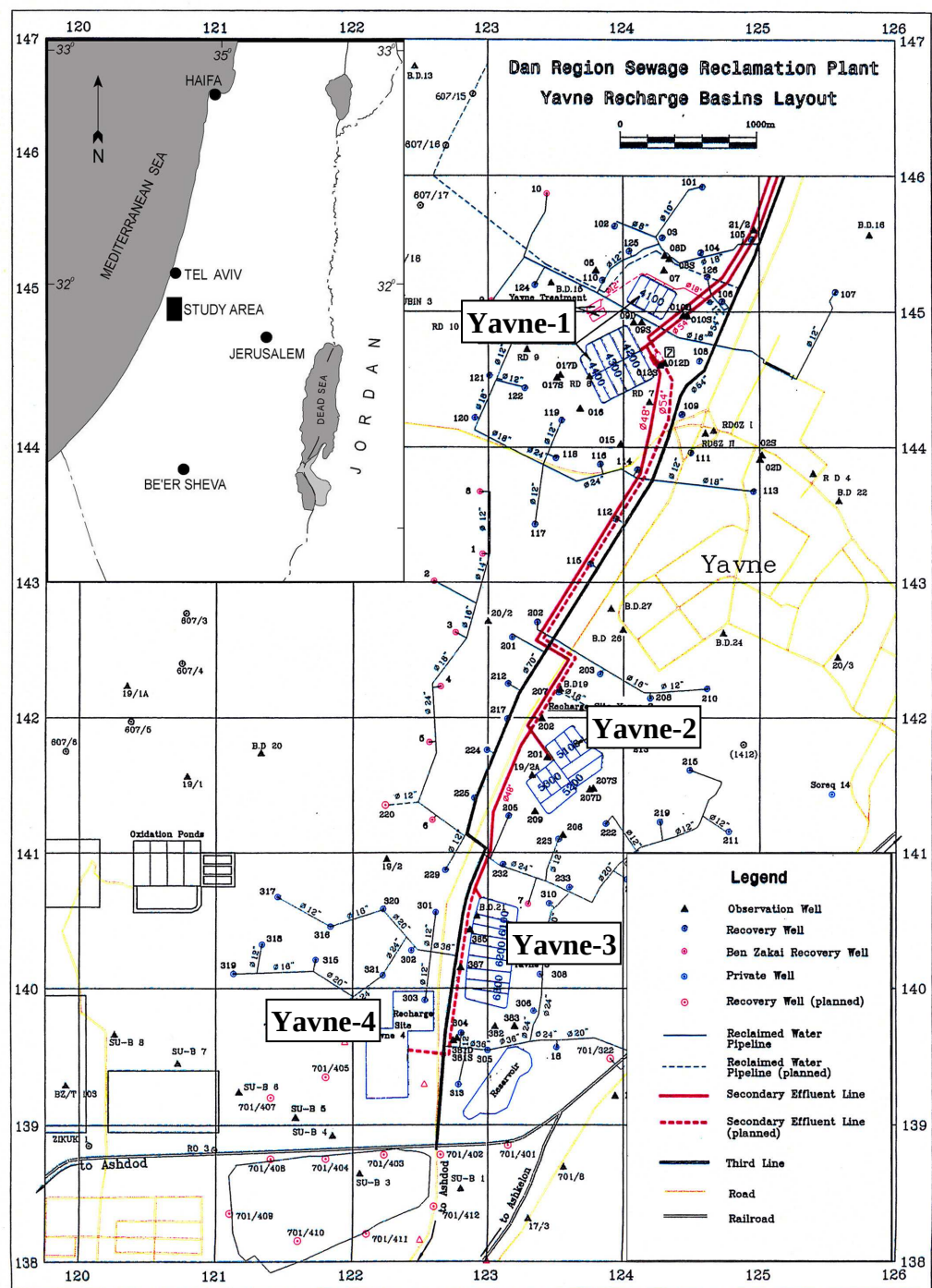


FIGURE 1.4: Location map of the Shafdan plant (map insert), the Yavne infiltration basins and the wells around them. Modified after: [Icekson-Tal et al., 2002](#).

1.4.1 The SAT system of the Shafdan

The SAT system of the Shafdan plant includes five infiltration basins (from north to south): Soreq, Yavne-1, Yavne-2, Yavne-3 and Yavne-4 (Fig. 1.4), which have been in operation since 1977, 1987, 1988, 1996 and 2003, respectively. Each basin covers an area of about 200,000 m² and is divided into about 10 sub-basins. The sub-basins are flooded alternately in cycles of 3-5 days. The drying periods between the floodings (about 1 day) maintain the high infiltration rates through the upper soil layer, and allow oxygen to penetrate into the soil (Idelovitch et al., 2003). In addition, plowing of the basins, which is done once in two weeks, breaks the soil biofilms and enhances the aeration of the upper soil. The water load applied in each flood varies between 30 and 100 cm, depending on the infiltration rate of each sub-basin.

The effluents are recovered from the aquifer by a series of production wells, located in two rings around each infiltration basin; the inner ring pump 100% effluents whereas the outer one produce a mixture of effluents and fresh water from the regional aquifer while creating a hydrological depression (Guttman et al., 2002). This low water level buffer zone isolates the area in the aquifer that contains effluents and prevents their spreading into the regional aquifer.

The quality of the effluents after the SAT is greatly improved and they are approved by the Ministry of Health for unrestricted irrigation and incidental drinking. Removal efficiency of above 70% is attained for the following components: suspended solids, organic matter, ammonium and organic nitrogen, phosphorus, fluoride, iron, nickel and cyanide; moderate removal efficiency (40-70%) is attained for detergents, phenols and mercury (Icekson-Tal et al., 2002).

The present research focused on the geochemical evolution of the water and the Mn mobilization in the SAT system of Yavne-2 basin, which began operating in 1988 and has the highest Mn concentrations among the five infiltration basins of the Shafdan plant.

1.4.2 Hydrogeologic background

The SAT system of the Shafdan plant utilizes an area of about 30 km² of the coastal plain aquifer of Israel. The geological section of the aquifer comprises alternating sands,

calcareous sandstones (Kurkar), red loams (Hamra) and marine clays, all of Pleistocene age (Issar, 1961, 1968), reaching a total thickness of up to 200 m (Ecker, 1999; Fig. 1.5). The aquifer is underlain by the thick Yafo Formation shale aquiclude of Pliocene age, which is part of the Sagiye Group (Gvirtzman, 1970). The aquifer is essentially phreatic, but clayey layers divide it vertically into several sub-aquifers. Melul, 1988 divided the aquifer into four main sub-aquifers (A-D, from top downward) that are distributed laterally from the shoreline to 5-10 km inland. In addition, local clayey lenses form vertical hydrologic partitions, resulting in different water table levels and different chemical and isotopic compositions of the water in the overlying and underlying sand units (Nativ and Weisbrod, 1994). However, the nature of these separations is spatially variable.

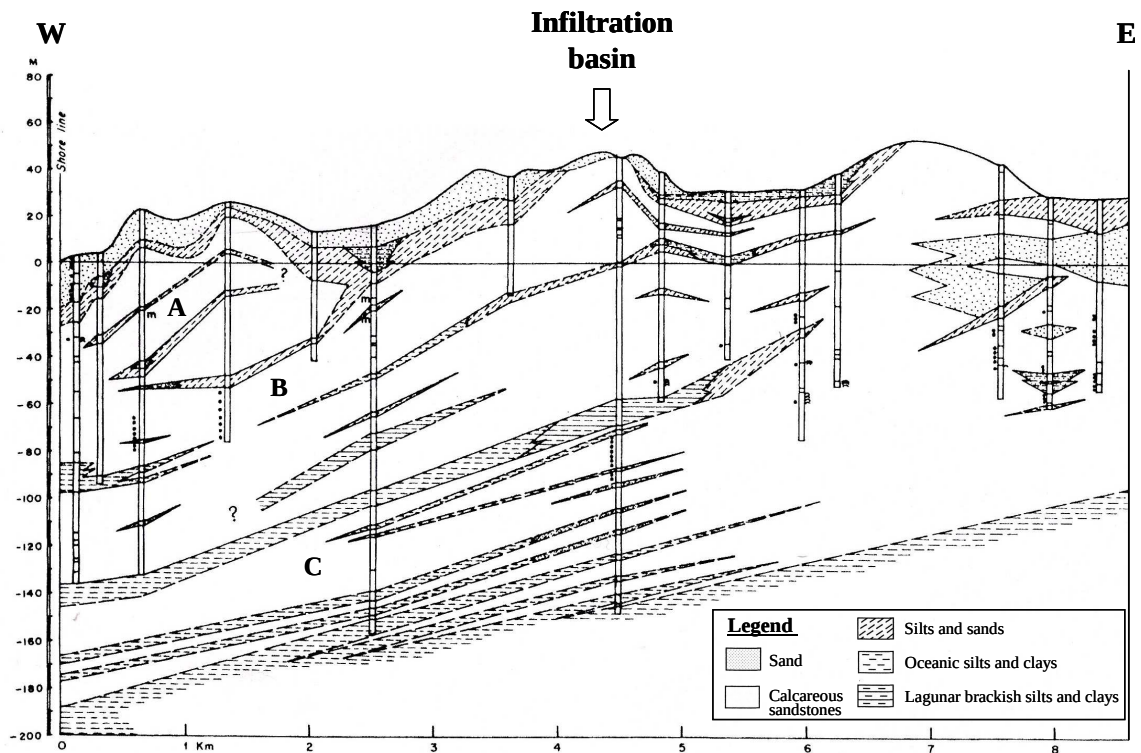


FIGURE 1.5: A geological section of the coastal plain aquifer of Israel in the Shafdan area. From: Ecker, 1999, Strip No. 18-19.

The aquifer is recharged directly by winter precipitation of about $0.5 \text{ m}\cdot\text{y}^{-1}$. Under undisturbed conditions, the groundwater flows from the foothills in the east to the sea in the west. The artificial recharge of the aquifer under the SAT system of the Shafdan plant and the local and regional pumping regime changed the flow pattern of the groundwater significantly, as described below.

The infiltration basins, located 3-5 km inland of the coastline, were excavated into dunes underlain by an elevated calcareous sandstone (Kurkar) ridge (Fig. 1.5). In this area, sub-aquifer B reaches the surface and is about 100 m thick, thus the SAT system utilizes this sub-aquifer. The thickness of the vadose zone below the infiltration basins is 30-40 m. The hydraulic loading of the effluents in the basins varies between 80 and 150 $\text{m}\cdot\text{y}^{-1}$, depending on the infiltration capacity of each basin (Icekson-Tal et al., 2003a). This huge amount of water that recharges the aquifer through relatively small areas forms hydrological mounds below the infiltration basins. The rings of production wells around each infiltration basin create a low water-level buffer zone between the SAT system and the regional aquifer. Generally, the shape of the water-level depression at the buffer zone is asymmetric, with sharp gradients towards the infiltration sites and low gradients towards the regional aquifer, upstream (Guttman et al., 2002). Proper control of this buffer zone shape minimizes the freshwater losses which are required for the efficient isolation of the reclaimed effluents from the main body of the aquifer. These buffer zones are located some 1-2 km away from the center of the infiltration basins.

The infiltration rates in the infiltration basins vary between 0.6 $\text{m}\cdot\text{d}^{-1}$ and 3 $\text{m}\cdot\text{d}^{-1}$ (Schweky, 1982; Michail et al., 1989). These rates are significantly affected by the quality of the effluents as well as by their temperature; the infiltration rates are highest during the summer whereas during the winter the rates decrease by 30-50% (Schweky, 1982; Lin et al., 2003).

1.4.3 The Yavne-2 infiltration basin

The Yavne-2 infiltration basin started operating in 1988 and since then has treated about 500 MCM of effluents. The annual volume of effluents that recharge through the Yavne-2 infiltration basin varies between 20 and 30 MCM, equivalent to a hydraulic load of 110-170 $\text{m}\cdot\text{y}^{-1}$ (Icekson-Tal et al., 2002). Generally, the annual volume of the recovered effluents, pumped by wells around the Yavne-2 basin, is similar to that of the recharged effluents, with some seasonal and inter-annual variations.

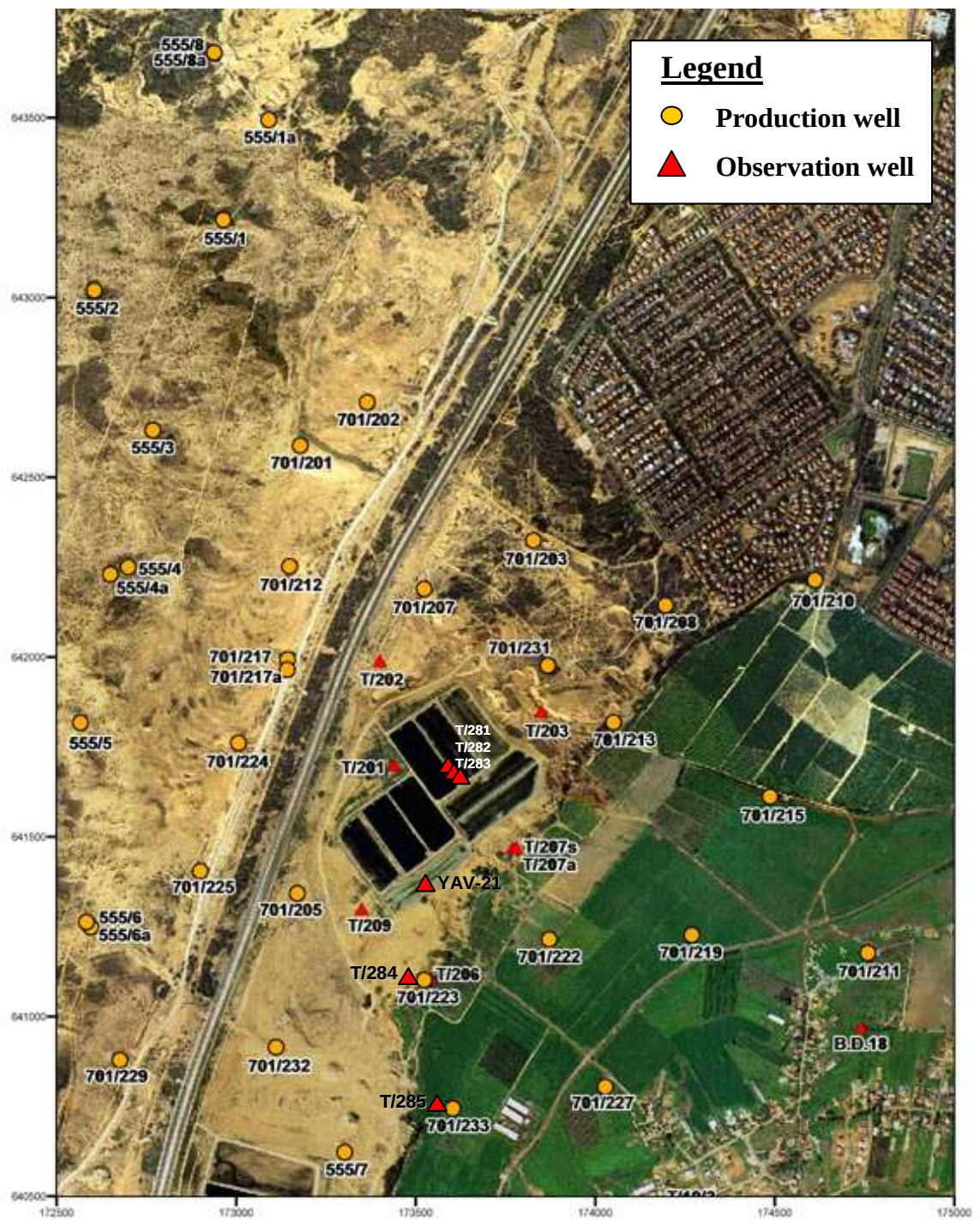


FIGURE 1.6: Orthophoto of the Yavne-2 infiltration basin and the observation and production wells around it.

1.4.4 Mn mobilization in the Shafdan plant

Mn mobilization in the Shafdan plant was first observed at the end of 2000 ([Halperin et al., 2003](#)). This was reflected by high concentrations of dissolved Mn (100-2200 ppb) in the reclaimed effluents and by precipitation of Mn oxides in the "third pipeline" which conveys the reclaimed effluents to the Negev. The appearance of Mn could not be attributed to a change in the Mn content of the recharged effluents, which remained constant (about 30 ppb), suggesting that Mn was mobilized within the SAT system, most probably due to reduction of Mn-oxides. By the end of 2002, Mn concentrations higher than 100 ppb were found in 19 production wells, including: 2 wells near the Soreq basin, 5 wells near the Yavne-1 basin, 11 wells near the Yavne-2 basin and one well near the Yavne-3 basin ([Halperin et al., 2003](#)).

Leaching of Mn from the sediments in the Shafdan infiltration basins was described by Banin et al. (2000, 2001, 2003). They found that a significant percentage of the original Mn was leached from the top soil down to a 10 m depth in Soreq and Yavne-3 infiltration basins as well as in an experimental pond in the same area, compared to the Mn content in an adjacent pristine dune. The leaching was explained by reductive dissolution of Mn-oxides due to low redox potential prevailing under the basins' surface during the flooding periods. An experiment was carried out to follow the changes in the Mn content in the sediments along the upper two meters of the soil profile under an experimental pond at various stages of the effluent load. The results show that when first measured after 34 months of operation, the Mn content has decreased by 40-50% but did not change significantly thereafter ([Banin et al., 2000, 2001](#)). This indicates that the Mn leaching is a relatively rapid process, which attains equilibrium in the upper soil within the first few years of effluent recharge. Accumulation of Mn in deeper layers in the unsaturated zone below the infiltration basins was explained by Mn(II) adsorption and/or precipitation ([Banin et al., 2001](#); [Banin and Lin, 2003](#)).

1.5 Research objectives and significance

The overall aim of this study is to identify and quantify the processes that impact and control Mn mobilization in a calcareous-sandstone aquifer recharged by water enriched with organic matter.

Accordingly, the more specific objectives of this study are:

- Identify and quantify the geochemical processes that dictate the chemical composition, and in particular Mn concentrations, of the groundwater in the aquifer and specifically of the recovered effluents.
- Map the different geochemical processes that take place in the aquifer, and determine whether they occur in the vadose zone and/or in the aquifer.
- Identify and quantify the processes that retard the mobility of reduced Mn^{2+} in the aquifer, including adsorption and precipitation of MnCO_3 .
- Describe the geochemical evolution of recharged effluents during their flow in the SAT system of the Shafdan plant.
- Formulate a conceptual model to describe the mobilization of Mn within the SAT system of the Shafdan plant.

The present study investigates and describes for the first time the severe degradation of the quality of recovered effluents from a SAT system due to drastic Mn concentration increase. Therefore, the research may be important for a better understanding of similar systems world-wide, and in predicting processes that may cause a significant degradation of groundwater quality.

In addition, the present study has a practical implication. The precipitation and accumulation of Mn oxides in the pipelines, which convey the recovered effluents, result in clogging and destruction of the irrigation systems belonging to the farmers, who are the end-users of the water. Thus, identifying and quantifying the sources, processes and conditions that are conducive for high Mn concentration in the recovered effluents are essential for establishing optimal solutions for this problem, and for suitable management of the SAT system of the Shafdan plant.

1.6 Outlines

The present dissertation examines the geochemical evolution of the water and Mn mobilization in a calcareous-sandstone aquifer recharged by organic-rich water. The research was conducted at Yavne-2 SAT system of the Shafdan plant, where high concentrations of Mn were found in the groundwater. An introduction to the dissertation is presented in Chapter 1. The methodology applied during the research is described briefly in Chapter 2 and in detail in the following chapters. The geochemical characterization of the effluents and the hydrological set-up of Yavne-2 are described in Chapter 3. The Mn inventory in the sediment column of the aquifer and its speciation are presented in Chapter 4. These quantities were evaluated by a series of Mn extractions from sediments that were sampled along three wells drilled at different distances from the infiltration basin. Chapter 5, which was published as an article in "Environmental Science and Technology", includes a general description of the geochemical evolution of the effluents and of Mn mobilization in the Yavne-2 SAT system, a mass balance between the cumulative Mn loads recharged into and recovered from the aquifer, and an estimation of the Mn retardation factor using two independent methods. Chapter 6 discusses the main water-rock interactions that take place during recharge of effluents into a sandy aquifer. This discussion is based on the results of column experiments, which were designed to simulate the recharge of effluents into a suboxic calcareous-sandstone aquifer, and on field evidences from the wells around Yavne-2 infiltration basin. In Chapter 7, an analysis is presented of the breakthrough behavior of reduced manganese in a sandy aquifer under suboxic conditions. This breakthrough behavior was investigated by column experiments (mentioned above) with different Mn concentrations and analyzed by an analytical model and a numerical model. Finally, the findings and conclusions that emerge from the study are integrated and summarized in Chapter 8, and a schematic conceptual model of Mn mobilization in an aquifer recharged by organic-rich water is provided.

Chapter 2

Methods

2.1 Field methods

- *Sampling of recharged effluents* - The recharged effluents were sampled directly from the infiltration basin. The effluents present within the vadose zone were sampled using ceramic cups installed at various depths between 0.5 and 9 m (Figs. 2.1 - 2.3). Water from the cups was pumped by a peristaltic pump directly to 100 mL syringes from which the water was taken for different analyses. A few campaigns were carried out to sample the infiltrating effluents during a cycle of flooding and drying of the basin.
- *Sampling of groundwater* - All observation and production wells around the Yavne-2 infiltration basin were sampled for various chemical analyses in two annual campaigns, in 2004 and 2005. Selected wells were sampled more than twice, when specific questions needed an answer. In addition, groundwater was sampled from the new wells during and after the drilling.
- *Water-table measurement* - The static water table depth was measured whenever a well was sampled. The depth from a reference point (usually the tube edge) to groundwater was measured before sampling by a manual water level sensor. The water levels in the production wells were measured in a designated side pipe after pumping breaks of at least 12 h (Fig. 2.4).
- *Drilling new observation wells* - Two observation wells were drilled in the center of the Yavne-2 infiltration basin using a rotary drill with drilling mud; well T/281

to 50 m depth and well T/282 to 60 m depth (Figs. 2.5, 2.6). Three additional wells were drilled with a dual system drilling instrument, which requires no drilling mud. This enabled reliable sampling of sediment and water along the aquifer profile (Figs. 2.7, 2.8). Well T/283 was drilled in the center of the infiltration basin (near T/281 and T/282) to a depth of 80 m; well T/284 was drilled 200 m from the basin also to a depth of 80 m; and well T/285 was drilled 560 m from the basin to a depth of 60 m. In addition, a shallow monitoring well was installed in an infiltration basin down to a perched water horizon at 7 m depth (well YAV-21). The location of all wells is shown in Fig. 1.6.

- *Sampling of sediments* - Sediments from the aquifer cross section were sampled during the drilling of wells T/283, T/284, and T/285. For lithological description samples were collected every 3 m into archive boxes; for chemical analyses samples were collected every 1.5 m into 50 mL vials, frozen on site with dry ice and transferred to the laboratory within 12 hours; and for clay content analyses about 0.5 kg of sediment samples were collected every 3 m into plastic bags. Pristine sediment for the column experiments was sampled at an undisturbed surface close to Yavne-2 basin.

2.2 Laboratory methods

- *Chemical analyses* - Most of the chemical analyses were carried out in the laboratories of the Geological Survey of Israel. Major cations and trace elements were analyzed on a Perkin Elmer Optima 3300 ICP AES. Anion concentrations were measured using a Dionex ICS-2000 ion chromatograph. Alkalinity (ALK) was determined by titration with 0.02N HCl. DIC was determined using two methods: 1. Collection and measurement of CO₂ obtained in a vacuum line by adding 1ml of H₃PO₄ to about 50 mL of the water sample. 2. Analyses on a ThermoFinnigan Delta Plus XP mass spectrometer connected to a Gas Bench II interface (Torres et al., 2005). DO was measured several times in the field with a gold electrode but commonly it was determined in the laboratory following the Winkler titration method. Ammonium was measured on a Turner Designs Aquafluor after Holmes et al., 1999. DOC and NKJT were measured at the Nesin laboratory of Mekorot Water Co. following the Standard Methods (Eaton et al., 1995).

- *Column experiments*- The column experiments were designed to simulate the geochemical evolution and Mn^{2+} mobilization during effluents' flow in a sandy aquifer under suboxic conditions (Figs. 2.9, 2.10). During each experiment, a solution similar in ionic composition to that of the effluents but with a variable Mn content was pumped through a column that was packed with a pristine red-brown sand from the Shafdan area. In order to simulate the suboxic conditions prevailing in the aquifer and to prevent oxidation of the soluble reduced Mn^{2+} , the artificial effluents container was continuously flushed with a gas mixture of N_2 (95%) and CO_2 (5%). The determination of the cation exchange capacity (CEC) of the sediments and the distribution of the adsorbed cations was conducted by leaching the sediments in the columns with a solution of $1\text{M NH}_4\text{NO}_3$ at $\text{pH}=7$.
- *Chemical analyses of sediments* - Total Mn concentration in the sediments was determined by the sintering method (Ilani et al., 1992). Different extractable forms of Mn, which include exchangeable + carbonate Mn, easily-reducible Mn oxides, and Mn bound to organic matter, were distinguished by sequential extraction in four steps, modified after Han and Banin, 1995. The content of the adsorbed cations in the sediments at the end of the experiments were determined during the first step of the sequential extraction, by batch extracting with a solution of $1\text{M NH}_4\text{NO}_3$ at $\text{pH}=7$.
- *Clay and carbonate contents in sediments* - The clay fraction ($< 2 \mu\text{m}$) in the sediments in several representative samples was determined by sedimentation method, based on Stokes law, following Black (1965). The clay mineral content in the sediment used in the column experiments was estimated by considering both the mineralogical composition and the chemical composition (e.g. Sandler et al., 2001). The CaCO_3 content in the sediments was determined by its dissolving with HNO_3 acid in a sealed canister and measuring the CO_2 pressure.

2.3 Data analysis

- *Historical data* - Historical data on volumes of recharged effluents and reclaimed groundwater and their chemical compositions were provided by the Mekorot Water Co.. Only samples with charge imbalance $<2\%$ were considered.

- All chemical analyses reported in the dissertation are presented in their accuracy degree of the analysis plus one digit (see Appendices 1-4, 6-14).
- *Mn breakthrough simulations* - Breakthrough curves of Mn^{2+} obtained in the column experiments were simulated with an analytical and a numerical models. The numerical model simulations were carried out using the "MATLAB" code, version 7.0 (see Appendix 15).



FIGURE 2.1: A drilling team preparing the installation of a ceramic cup.

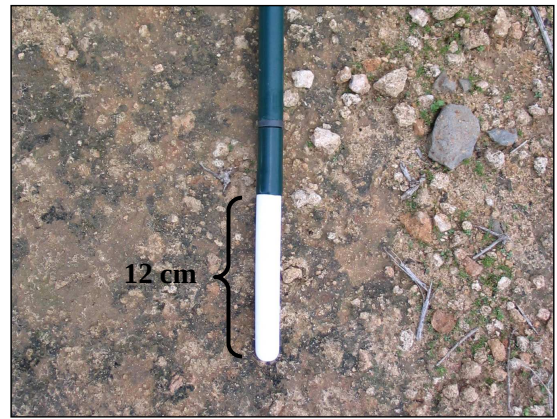


FIGURE 2.2: A ceramic cup.

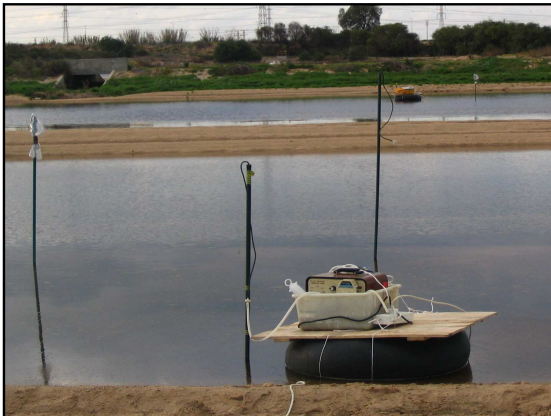


FIGURE 2.3: Sampling of water from ceramic cups using a peristaltic pump.



FIGURE 2.4: Water level measurement in a production well.



FIGURE 2.5: Drilling of wells T/281, T/282 using a rotary drill with drilling mud.



FIGURE 2.6: Observation well T/282.



FIGURE 2.7: Drilling wells T/283, T/284 and T/285, using a dual system drilling instrument. The cuttings are removed from the borehole by compressed air.



FIGURE 2.8: Installation of a 2" diameter PVC tube at the end of the drilling.

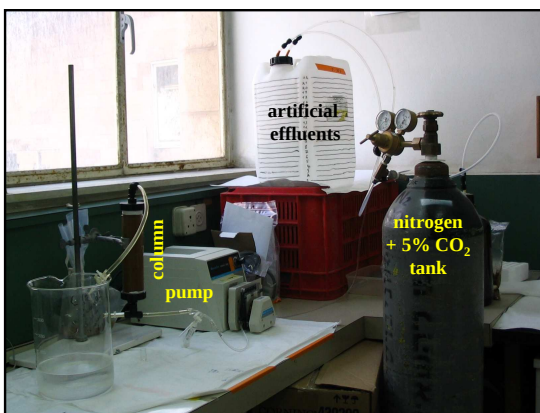


FIGURE 2.9: The column experiment system, simulated the geochemical evolution of effluents in the Shafdan aquifer.

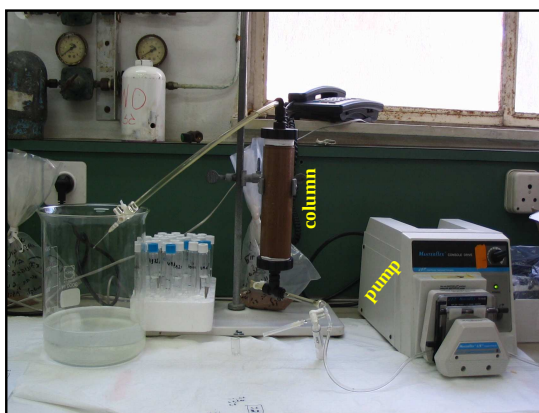


FIGURE 2.10: The column experiment system. Zoom on the peristaltic pump and experimental column.

Chapter 3

Geochemical and hydrological background - analysis of historical data and present findings

The present chapter summarizes the hydrological and geochemical conditions in Yavne-2 SAT system as interpreted from historical data collected and provided by Mekorot Water Co., which operates the Shafdan plant, and from recent data collected in the present study.

3.1 Hydrological characterization of the Yavne-2 basin

3.1.1 Aquifer water table

A map of the aquifer water table elevations beneath the Yavne-2 SAT system was constructed based on the static water table depths measured in the 2005 annual campaign (Appendix 2) and is presented in Fig. 3.1. A hydrologic high of several meters, resulting from the intensive effluent recharge, exists about 40 m below the basin surface. Further away, the water table level declines creating a trimmed cone which is steeper to the east and more moderate to the west. In the south, a hydrologic saddle is created due to recharge from the adjacent Yavne-3 basin. The water table level decreases towards

the outer circle of the production wells around the basin, forming hydrologic troughs between the SAT system and the surrounding regional aquifer.

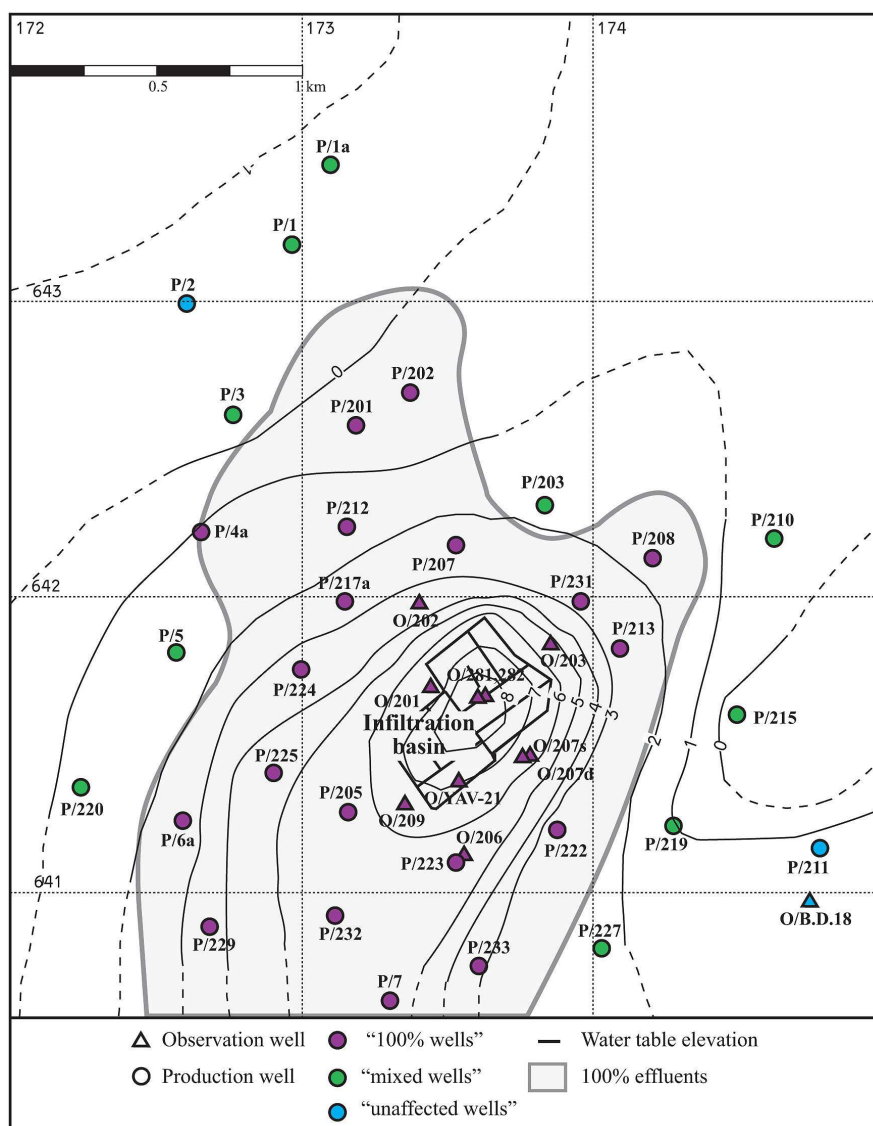


FIGURE 3.1: Water table elevation map of the Yavne-2 SAT system. The mixing ratios between the recharged effluents and the regional fresh groundwater, according to the Cl^- concentrations, are denoted by color.

3.1.2 The chemical expression for this hydrological structure

The hydrological structure dictates the flow directions in the aquifer and hence the mixing ratio between the recharged effluents and the regional fresh groundwater. Therefore, the chemical composition of the water helps understanding the hydrological system. Cl^- is used to estimate the mixing ratios between the recharged effluents (RE) and the regional fresh groundwater. Accordingly, all wells were divided into three groups (Fig. 3.1): 1. "100% wells" - wells assumed to produce 100% reclaimed effluents, having $\text{Cl}^- \geq 8.5 \pm 1.1 \text{ meq}\cdot\text{L}^{-1}$; 2. "Unaffected wells" - wells producing fresh groundwater from the regional aquifer. 3. "Mixed wells" - wells with Cl^- concentrations in-between, which depend on the degree of mixing between the two end members - fresh groundwater and effluents. This division corresponds to the locations of the wells; the "100% wells" are located within the hydrologic high, where groundwater flows from the basin outward, the "Mixed wells" form the hydrologic troughs, while the "Unaffected wells" are located beyond these troughs. An exception is well P/203, which is located on the hydrologic high but produces a mixed groundwater composition (Fig. 3.1). This well is quite deep and probably pumps also deep fresh water from sub-aquifer C.

3.1.3 Infiltration rates in the basin

A rough estimation of the effluent infiltration rates in the vadose zone can be obtained from the time it takes the effluents to appear in the ceramic cups at various depths after the basin above has been flooded. The effluents were found to reach a depth of 1 m within 2.5 h, a depth of 3.8 - 4.1 m after 16.5 - 21.5 h (three ceramic cups) and 8.9 and 9.0 m after 22.5 - 27 h (two ceramic cups). According to these, the infiltration rate varies between $0.2 \text{ m}\cdot\text{h}^{-1}$ and $0.4 \text{ m}\cdot\text{h}^{-1}$. Since the thickness of the vadose zone below the infiltration basin is about 40 m, it takes some 4 - 9 days for the RE to reach the aquifer. Infiltration through preferential flow paths within the vadose zone is probably more rapid. However, these values correspond to infiltration rates calculated from the water level drop in the infiltration basins vs. time during the drainage phase of flooding cycles (Schweky, 1982; Michail et al., 1989; Lin et al., 2003).

3.2 Geochemical evolution of groundwater with time

The chemical composition of the recharged effluents and of the groundwater pumped from the different wells since the onset of operation of Yavne-2 basin is described below (see Figs. 3.2 - 3.5 and Appendix 5). The processes that dictate the geochemical evolution of the effluents, until steady state is attained, are analyzed in detail in Chapter 6.

3.2.1 Major ions

The Cl^- concentrations in the 100% wells follow the RE concentrations, while the concentrations in the mixed wells vary in the range between the RE and the fresh groundwater concentrations (Fig. 3.2A). The fresh groundwater in the eastern side of the ridge, where the infiltration basin is located, (represented by well P/211, see location in Fig. 3.1) is more saline than the fresh groundwater in the western side (represented by well P/2). This spatial difference affects the compositions of the mixtures. The more saline composition to the east is due to intensive agricultural activity, whereas the western side is recharged only by rain water.

In general, the concentrations of SO_4^{2-} (Fig. 3.2B) and Na^+ (Fig. 3.3A) behave similarly to those of Cl^- ; the groundwater in the 100% wells attains the concentrations of the RE within the first years of operation, while the concentrations in the mixed wells are lower, depending on the degree of mixing with the fresh groundwater.

The concentrations of K^+ (Fig. 3.3B) and Mg^{2+} (Fig. 3.3D) in the 100% wells approach and attain the RE concentrations after a somewhat longer period. The K^+ and Mg^{2+} concentrations in the eastern unaffected wells are higher and similar, respectively, to the RE concentrations. Furthermore, some of the mixed wells have higher concentrations than those in the RE. Direct infiltration of irrigation water enriched in fertilizers is probably the cause for these higher K^+ and Mg^{2+} concentrations.

The Ca^{2+} concentrations in the 100% wells are higher by 1 - 2 $\text{meq}\cdot\text{L}^{-1}$ than those in the RE (Fig. 3.3C), indicating that CaCO_3 dissolves within the aquifer. This dissolution is not accompanied by a concurrent rise in alkalinity (Fig. 3.2C). An explanation for this incompatibility is presented later in Chapter 6.

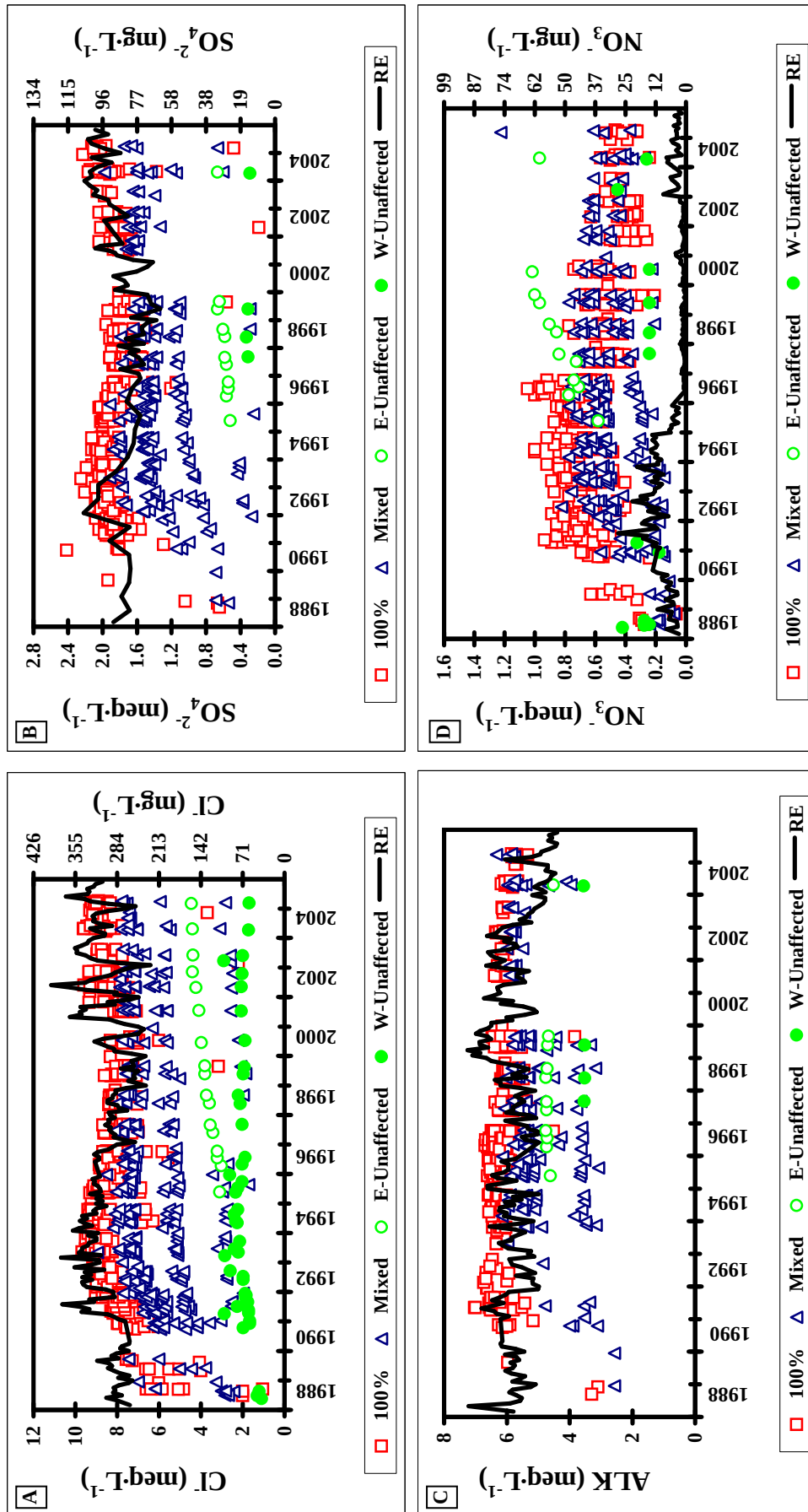


FIGURE 3.2: Concentrations of (A) Cl^{-} ; (B) SO_4^{2-} ; (C) ALK; and (D) NO_3^{-} , in the RE and the production wells surrounding the Yavne-2 basin during 1988-2005. 100% - wells that pump 100% effluents; Mixed - wells that pump a mixture of effluents and fresh water; E-Unaffected and W-Unaffected- wells that pump only fresh groundwater from the eastern side (well P/211) and western side (well P/2), respectively.

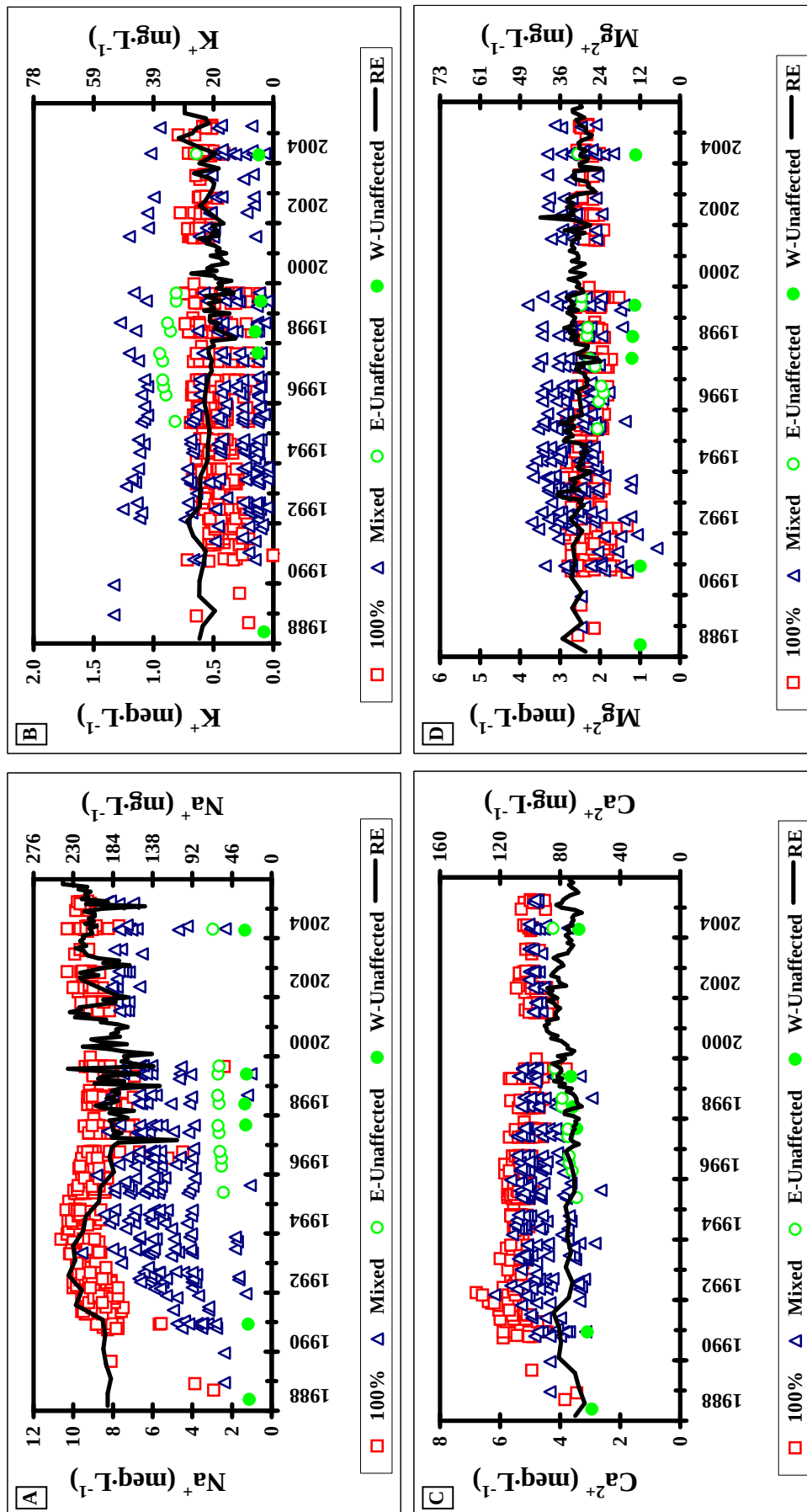


FIGURE 3.3: Concentrations of (A) Na^+ ; (B) K^+ ; (C) Ca^{2+} ; and (D) Mg^{2+} , in the RE and the production wells surrounding the Yavne-2 basin during 1988-2005. 100% - wells that pump 100% effluents; Mixed - wells that pump a mixture of effluents and fresh water; E-Unaffected and W-Unaffected- wells that pump only fresh groundwater from the eastern side (well P/211) and western side (well P/2), respectively.

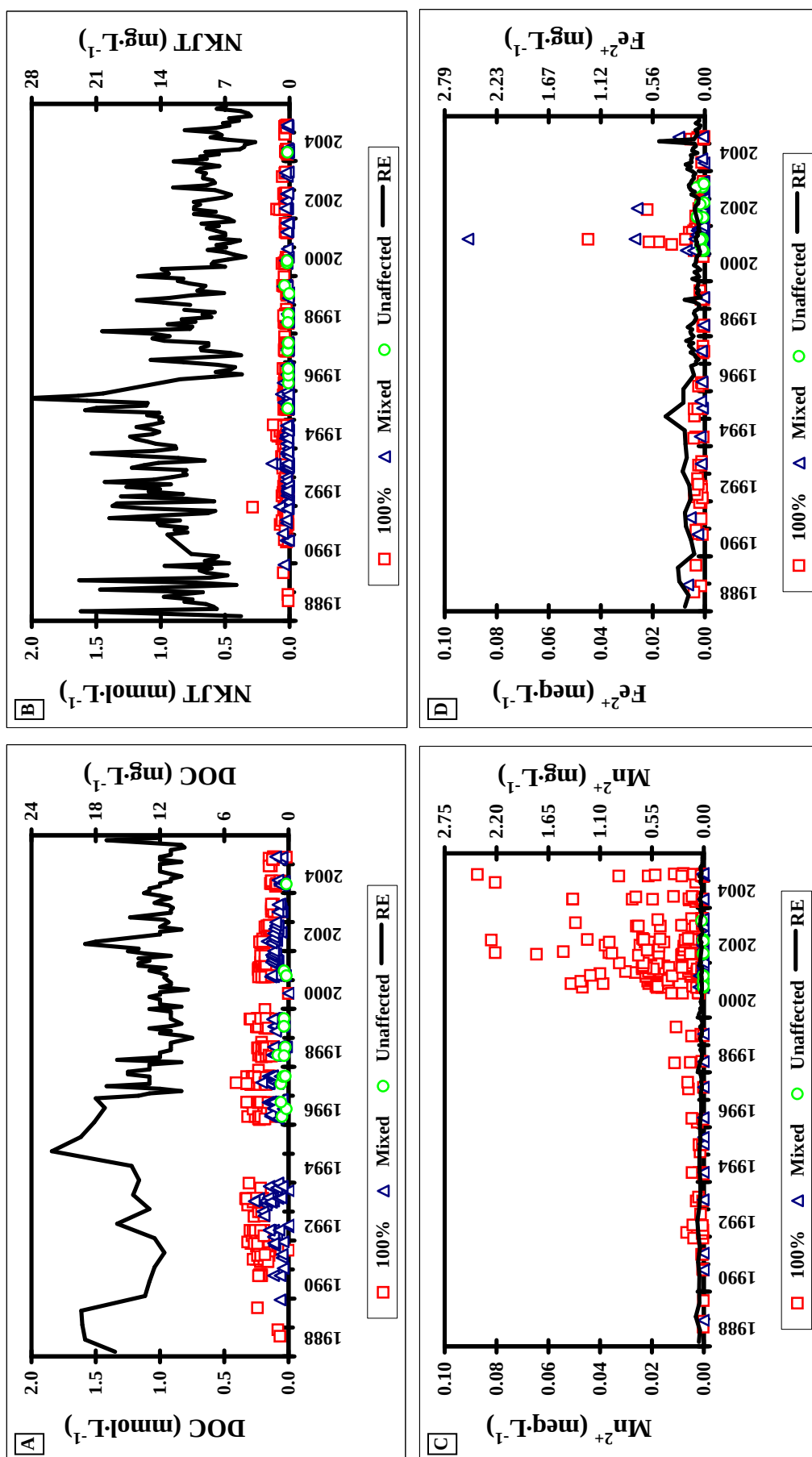


FIGURE 3.4: Concentrations of (A) dissolved organic carbon, DOC; (B) Kjeldahl-nitrogen (organic - N + NH₄⁺), NKJT; (C) Mn²⁺; and (D) Fe²⁺, in the RE and the production wells surrounding the Yavne-2 basin during 1988-2005. 100% - wells that pump 100% effluents; Mixed - wells that pump a mixture of effluents and fresh water; Unaffected - wells that pump only fresh groundwater.

The NO_3^- concentrations, a major anion in groundwater, is discussed in the following section.

3.2.2 Redox sensitive components

The main electron donors in the RE that drive the redox processes in the SAT system are organic matter and NH_4^+ . The dissolved organic carbon (DOC) and the Kjeldahl - nitrogen (NKJT), which include the organic - N and the NH_4^+ , drop from 0.8 - 1.5 $\text{mmol}\cdot\text{L}^{-1}$ and 0.5 - 1.5 $\text{mmol}\cdot\text{L}^{-1}$ in the RE to less than 0.3 $\text{mmol}\cdot\text{L}^{-1}$ and 0.06 $\text{mmol}\cdot\text{L}^{-1}$ in the groundwater, respectively (Figs. 3.4A, 3.4B). These significant decreases in concentrations indicate that intensive organic matter oxidation and nitrification of NH_4^+ take place in the SAT system. Both processes consume oxygen and reduce its concentrations in the aquifer. The nitrification process results in an increase in NO_3^- concentrations in the 100% wells by about 0.3 - 0.6 $\text{mmol}\cdot\text{L}^{-1}$, compared to the RE concentrations (Fig. 3.2D), while the total - N concentrations remain similar to that in the RE (Fig. 3.5). Yet, before 1996 and to a lesser extent later, the total - N concentrations in the 100% wells were lower than the concentrations in the RE, suggesting that some of the NH_4^+ is either adsorbed or denitrified in the SAT system. The high NO_3^- concentrations in the eastern unaffected wells and in some of the mixed wells are not due to the process in the SAT but are a result of the agricultural activity mentioned above.

In the RE, the concentrations of Mn^{2+} and Fe^{2+} are low and constant at about 0.001 $\text{meq}\cdot\text{L}^{-1}$ and 0.004 $\text{meq}\cdot\text{L}^{-1}$, respectively (Figs. 3.4C, 3.4D). The Mn^{2+} concentrations in the 100% wells increased significantly since the end of 2000, or even a few years earlier (see Chapter 5), to values between 0.004 $\text{meq}\cdot\text{L}^{-1}$ and 0.08 $\text{meq}\cdot\text{L}^{-1}$ (0.1 - 2.2 $\text{mg}\cdot\text{L}^{-1}$; Fig. 3.4C). This increase was caused by, and indicates Mn mobilization within the SAT system, which is the main topic of the present study. In the mixed and unaffected wells, the Mn^{2+} concentrations remain low.

The Fe^{2+} concentrations in all wells are mostly lower than those in the RE (Fig. 3.4D). This indicates that the SAT system has not yet approached the low redox conditions that enable Fe reduction. The few measurements of higher concentrations are sporadic in time and space and may have resulted from sampling or analytical errors.

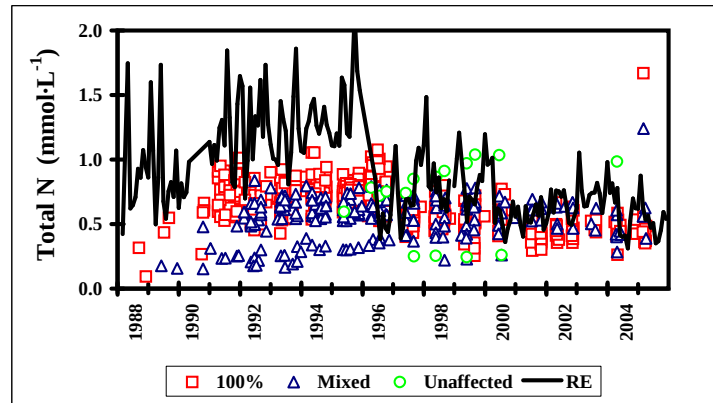


FIGURE 3.5: Total N concentrations in the RE and the production wells surrounding the Yavne-2 basin during 1988-2005.

3.3 Geochemical composition of groundwater as a function of distance from the infiltration basin

The two annual sampling campaigns, during which all observation and production wells around the Yavne-2 basin were sampled, lasted less than 2 weeks each, thereby providing a simultaneous geochemical snap-shot of the entire SAT system. The measured solute concentrations from both campaigns versus distance of the wells from the infiltration basin margin are presented in Figs. 3.6 - 3.8 and in Appendices 1, 2.

During 2004 - 5, the concentrations of Cl^- , SO_4^{2-} , Na^+ , K^+ and Mg^{2+} in the 100% wells were similar to those of the RE and did not change along the water flow path (Figs. 3.6, 3.7). The similarity implies that presently the SAT system is in equilibrium with respect to these components. It is different from the situation which prevailed during the first years of operation, when mixing and cation exchange modified the major ion composition (see Figures 3.2, 3.3). The lower concentrations in the farther mixed well, located to the north-west of the basin, are attributed to the low concentrations in the fresh groundwater in the western side of the aquifer. The Ca^{2+} and alkalinity concentrations were higher in the 100% wells, compared to the RE, by about $1 - 1.5 \text{ meq}\cdot\text{L}^{-1}$ and $0.5 - 1 \text{ meq}\cdot\text{L}^{-1}$, respectively, with no significant change along the flow path (Figs. 3.6C, 3.7C). This suggests that CaCO_3 dissolution, which controls the increase in Ca^{2+} and alkalinity, attains steady state already in the early stage of the flow.

The NO_3^- concentrations measured in the RE were $<0.03 \text{ meq}\cdot\text{L}^{-1}$ ($<2 \text{ mg}\cdot\text{L}^{-1}$), while the concentrations in groundwater were between $0.3 \text{ meq}\cdot\text{L}^{-1}$ and $0.6 \text{ meq}\cdot\text{L}^{-1}$ (Fig.

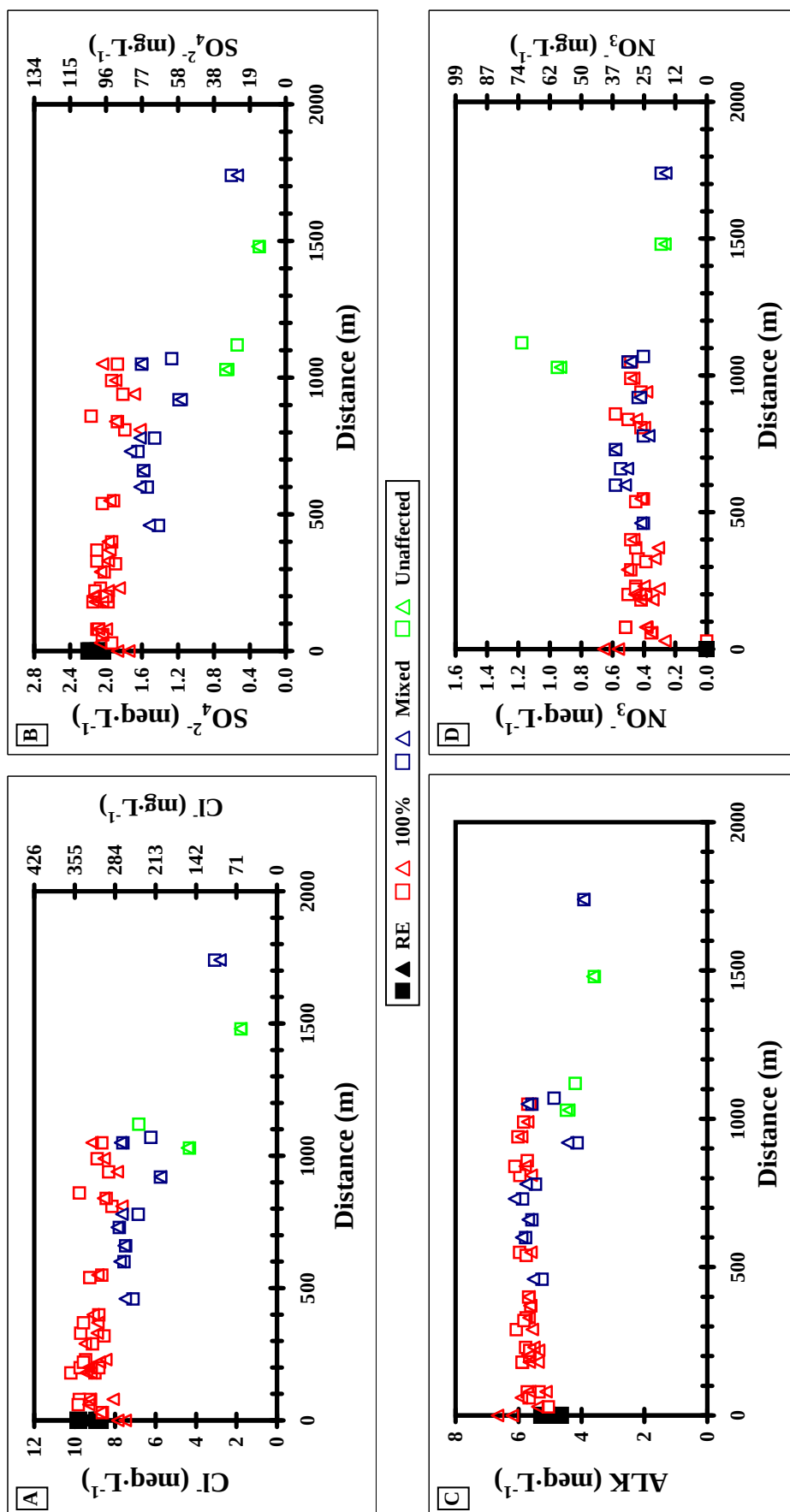


FIGURE 3.6: Concentrations of (A) Cl^- ; (B) SO_4^{2-} ; (C) ALK; and (D) NO_3^- versus distance from the infiltration basin margin in the RE and the wells (observation and production) surrounding the Yavne-2 basin, measured in the 2004 (squares) and 2005 (triangles) monitoring campaigns. 100% - wells that pump 100% effluents; Mixed - wells that pump a mixture of effluents and fresh water; Unaffected - wells that pump only fresh groundwater.

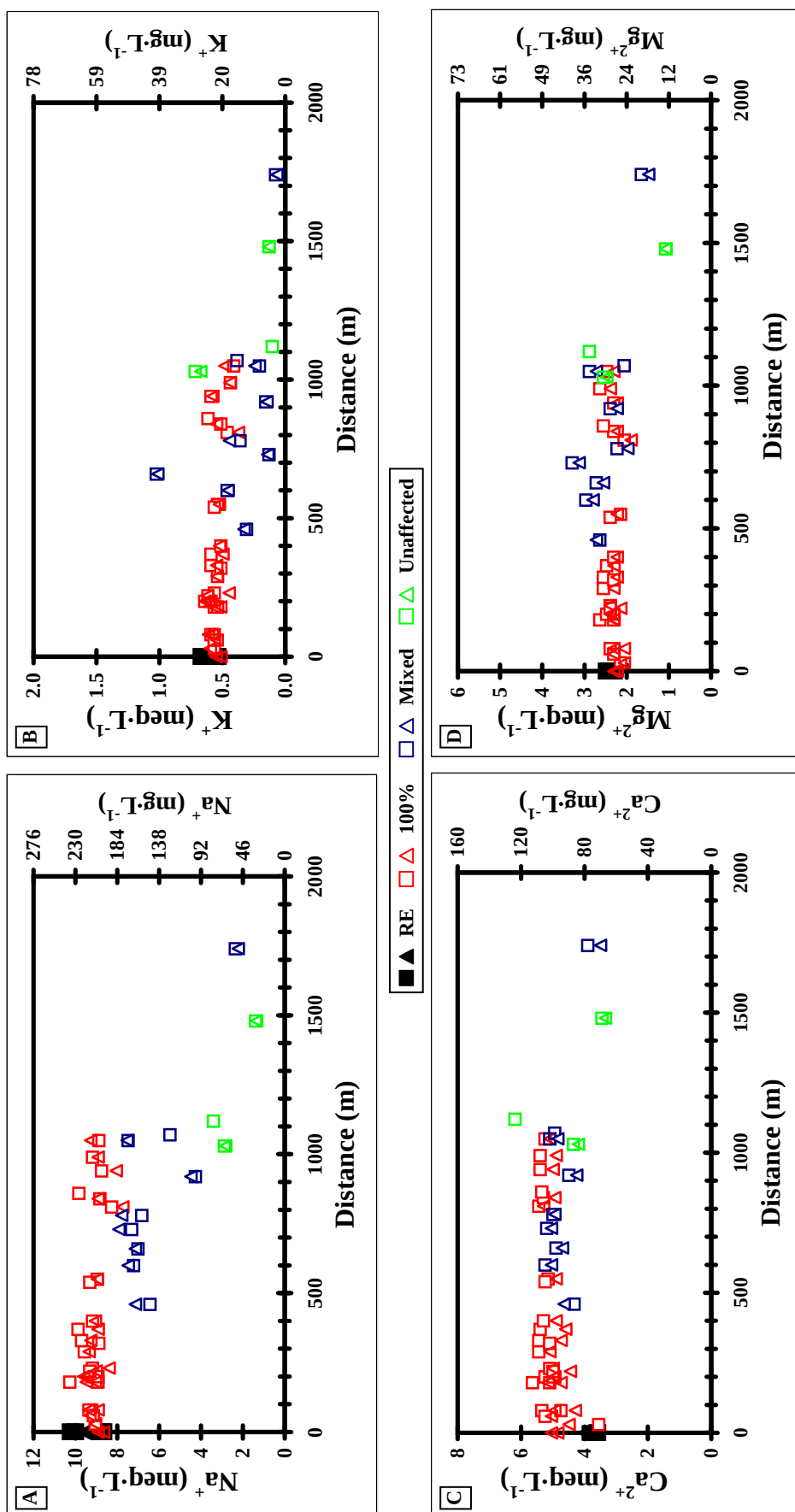


FIGURE 3.7: Concentrations of (A) Na^+ ; (B) K^+ ; (C) Ca^{2+} ; and (D) Mg^{2+} versus distance from the infiltration basin margin in the RE and the wells (observation and production) surrounding the Yavne-2 basin, measured in the 2004 (squares) and 2005 (triangles) monitoring campaigns. 100% - wells that pump 100% effluents; Mixed - wells that pump a mixture of effluents and fresh water; Unaffected - wells that pump only fresh groundwater.

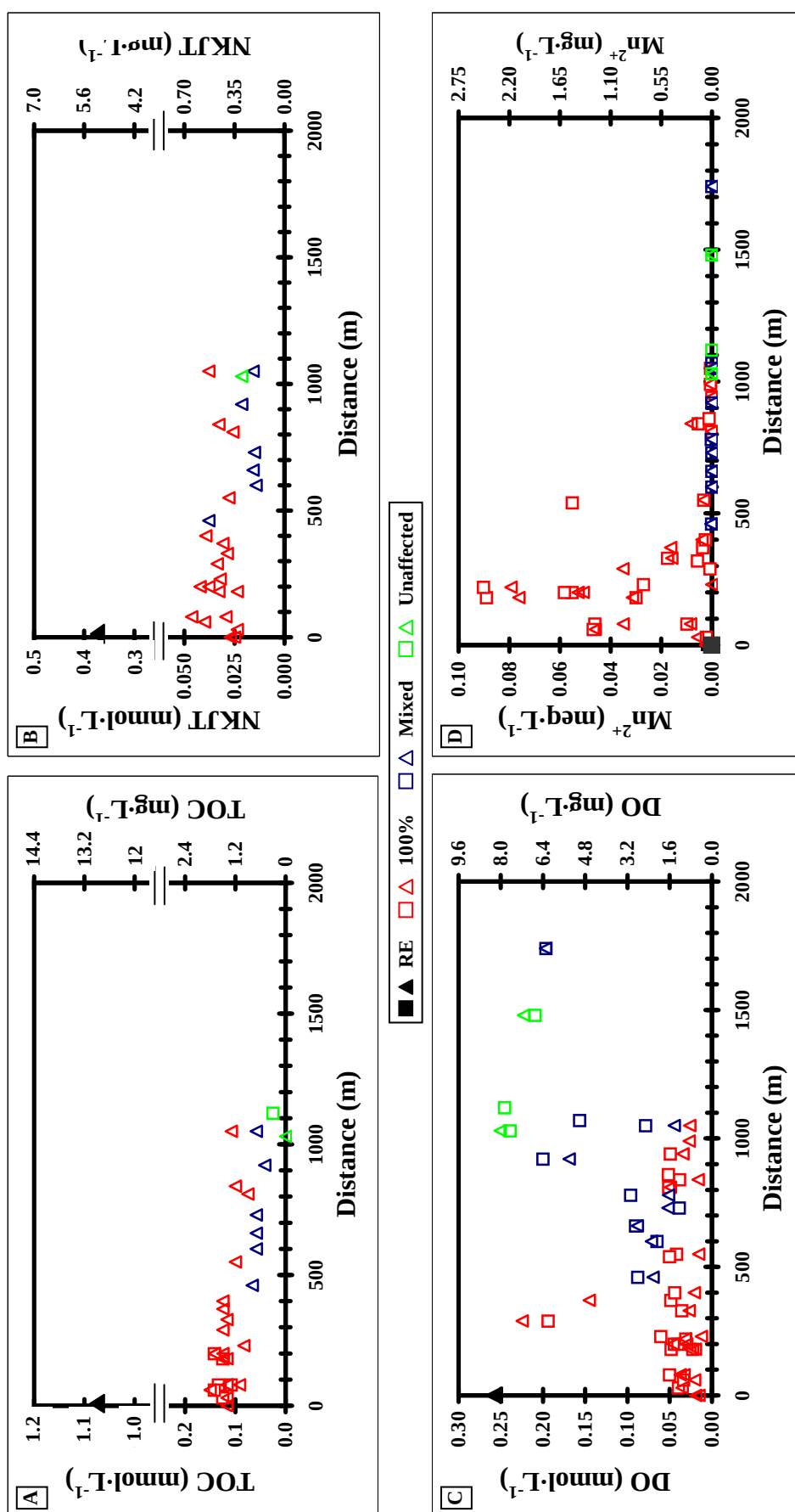


FIGURE 3.8: Concentrations of (A) total organic carbon, TOC; (B) Kjeldahl-nitrogen (organic - N + NH₄⁺, NKJT); (C) dissolved oxygen, DO; and (D) Mn²⁺ versus distance from the infiltration basin margin in the RE and the wells (observation and production) surrounding the Yavne-2 basin, measured in the 2004 (squares) and 2005 (triangles) monitoring campaigns. 100% - wells that pump 100% effluents; Mixed - wells that pump a mixture of effluents and fresh water; Unaffected - wells that pump only fresh groundwater .

3.6D). The high NO_3^- concentrations were observed already in the two shallow wells drilled in the center of the infiltration basin (T/281 and T/282). This implies that the nitrification process, which causes the NO_3^- concentration increase, occurs in the vadose zone. The relatively constant concentrations along the flow path within the aquifer suggest that denitrification, if it takes place, is a minor process which could not be detected in the analysis of NO_3^- .

The drop in total organic carbon (TOC) and NKJT concentrations in the 100% wells compared to their RE concentrations (Figs. 3.8A, 3.8B) was identified below the infiltration basin in wells T/281 and T/282. This indicates that most (about 90%) of the recharged organic matter is oxidized in the vadose zone during the early stages of infiltration. A further but slight decrease in the concentrations along the flow path is identified, which suggests additional, but minor, organic matter oxidation below the water table.

The dissolved oxygen (DO) measured in the RE in the infiltration basin was $0.26 \text{ mmol}\cdot\text{L}^{-1}$ ($8.3 \text{ mg}\cdot\text{L}^{-1}$), i.e. about saturation value, while its concentrations in the 100% wells were less than $0.06 \text{ mmol}\cdot\text{L}^{-1}$ ($<2 \text{ mg}\cdot\text{L}^{-1}$; Fig. 3.8C). Daily variation of the DO concentrations, in the range of $0.16 - 0.53 \text{ mmol}\cdot\text{L}^{-1}$ ($5 - 17 \text{ mg}\cdot\text{L}^{-1}$), was observed in the infiltration basin, resulting from photosynthesis and respiration. However, the DO depletion is attributed to the organic matter oxidation and nitrification, which take place mainly in the vadose zone. In the fresh groundwater, the DO concentrations are also around the saturation value ($0.21 - 0.25 \text{ mmol}\cdot\text{L}^{-1}$). Accordingly, the mixed wells were found to have intermediate DO values (between those of the 100% and the unaffected wells).

High Mn^{2+} concentrations were measured in the 100% wells that are located within a radius of about 500 m from the basin (Fig. 3.8D). No correlation was found between the Mn^{2+} concentration and the distance from the basin within this circle. 100% wells located farther from the basin had lower Mn^{2+} concentrations, similar to the background concentrations in the aquifer. This implies that retardation of Mn^{2+} mobilization is operative within the aquifer that contains 100% effluents. The Mn^{2+} concentrations in the mixed wells are similar to those in the unaffected wells, $<0.0004 \text{ meq}\cdot\text{L}^{-1}$ ($<0.01 \text{ mg}\cdot\text{L}^{-1}$). The mechanism of mobilization and retardation of the Mn in the aquifer is discussed in depth in Chapter 7.

3.4 Geochemical evolution of the effluents in the vadose zone

The geochemical evolution of the effluents in the upper part of the vadose zone was examined by concurrent sampling of the RE in the basin and the infiltrating effluents at various depths between 0.5 m and 9 m below the basin surface. Due to the limited water volume obtained by the ceramic cups, the concentrations of the organic components and the DO could not be determined. The results of the sampling campaigns are presented in Figs. 3.9 - 3.11 and in Appendix 6.

In general, the major ions: Cl^- , SO_4^{2-} , Na^+ , K^+ and Mg^{2+} do not change during the infiltration of the effluents along the vadose zone and their concentrations are dictated by the concentration of the RE (Figs. 3.9, 3.10). The Ca^{2+} and alkalinity concentrations in the infiltrating effluents varied between the concurrent RE concentrations and concentrations higher by 0.5 - 2 $\text{meq}\cdot\text{L}^{-1}$ (Figs. 3.9C, 3.10C). An increase in their concentrations was observed in the second sampling campaign, while in the first one there was no change. In addition, no clear increase in the concentrations with depth was observed. These may indicate that CaCO_3 dissolution takes place in the vadose zone in varying intensities, which may depend on the infiltration velocity, i.e., the contact time of the effluents with the sedimentary CaCO_3 , and on the effluents' temperature and pH.

The NO_3^- concentrations in the infiltrating effluents were usually higher than those in the RE and varied over a wide range, between 0.12 $\text{meq}\cdot\text{L}^{-1}$ and 1.34 $\text{meq}\cdot\text{L}^{-1}$ (Fig. 3.9D). Thus, nitrification must be a rapid process which occurs already in the upper part of the vadose zone while its intensity is highly variable. Rapid nitrification is suggested also by a significant decrease, of 2 - 3 orders of magnitude, in the NH_4^+ concentrations in the infiltrating effluents compared to those in the RE (Fig. 3.11A).

The Mn^{2+} and Fe^{2+} concentrations in the infiltrating effluents were, in most cases, lower than those in the RE (Figs. 3.11B, 3.11C). These deficits may point to oxidation and precipitation of these elements to solid oxides or adsorption onto the sediments. No evidence was found for recent reductive dissolution of Mn - oxides and Mn^{2+} mobilization in the upper part of the vadose zone.

In summary, it is clear that presently the chemical composition of the major ions in the effluents does not change during their flow in the SAT system, except Ca^{2+} and

alkalinity which increase due to CaCO_3 dissolution. This indicates that the SAT system attained a steady state with respect to the chemical composition of the RE. Oxidation of organic matter and nitrification results in a decrease of the TOC, NKJT and DO concentrations and an increase in the NO_3^- concentration, mainly within the vadose zone. High Mn^{2+} concentrations, which appear in the 100% wells since the end of 2000, indicate Mn mobilization in the SAT system, recently within the aquifer. Low Mn^{2+} concentrations in a few farther 100% wells imply on a geochemical process retards the Mn^{2+} mobilization within the aquifer that contains 100% effluents.

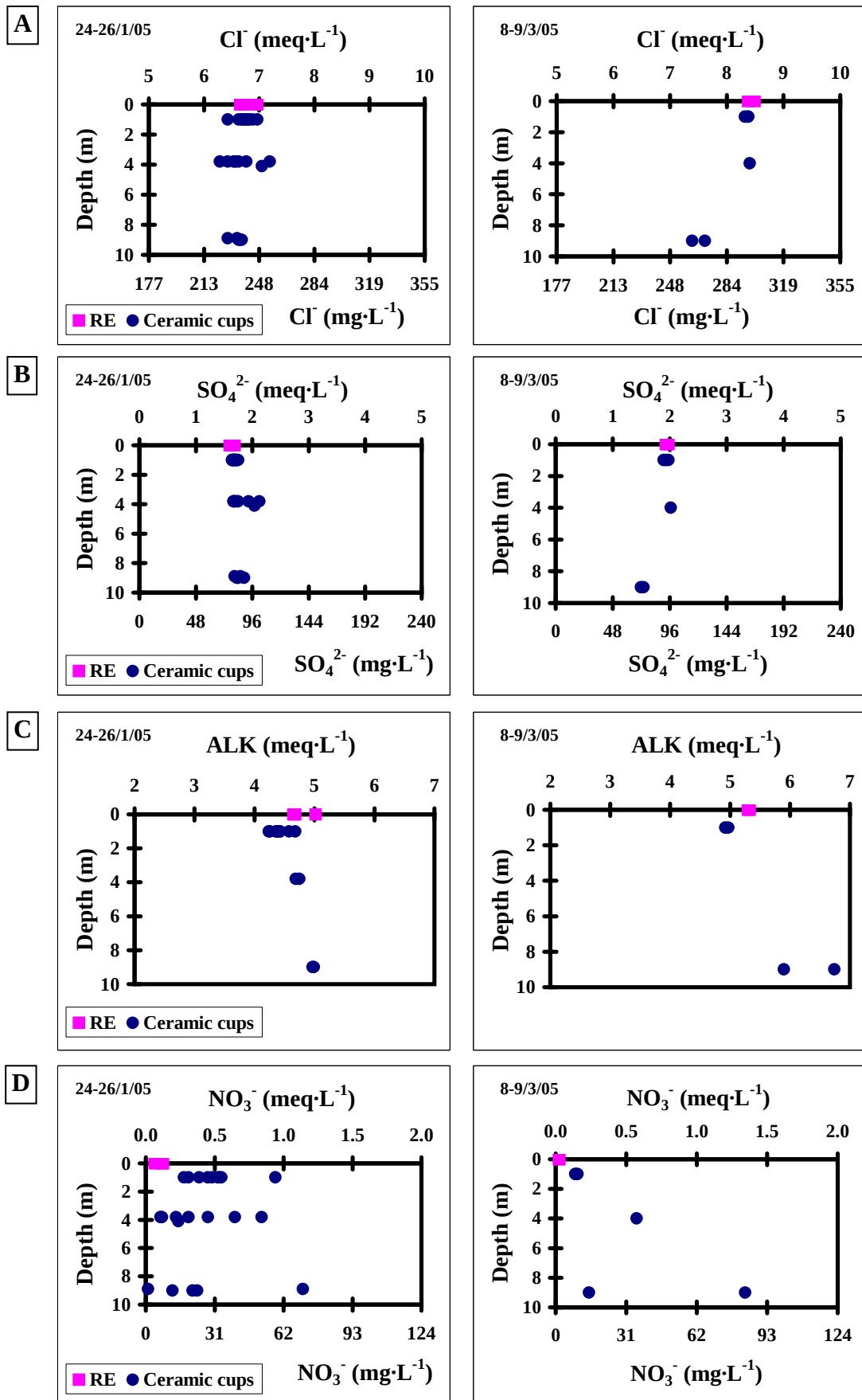


FIGURE 3.9: Concentrations of (A) Cl^- ; (B) SO_4^{2-} ; (C) ALK; and (D) NO_3^- in the RE and in the infiltrating effluents in the upper 9 m of the vadose zone below the basin, sampled from ceramic cups during two sampling campaigns.

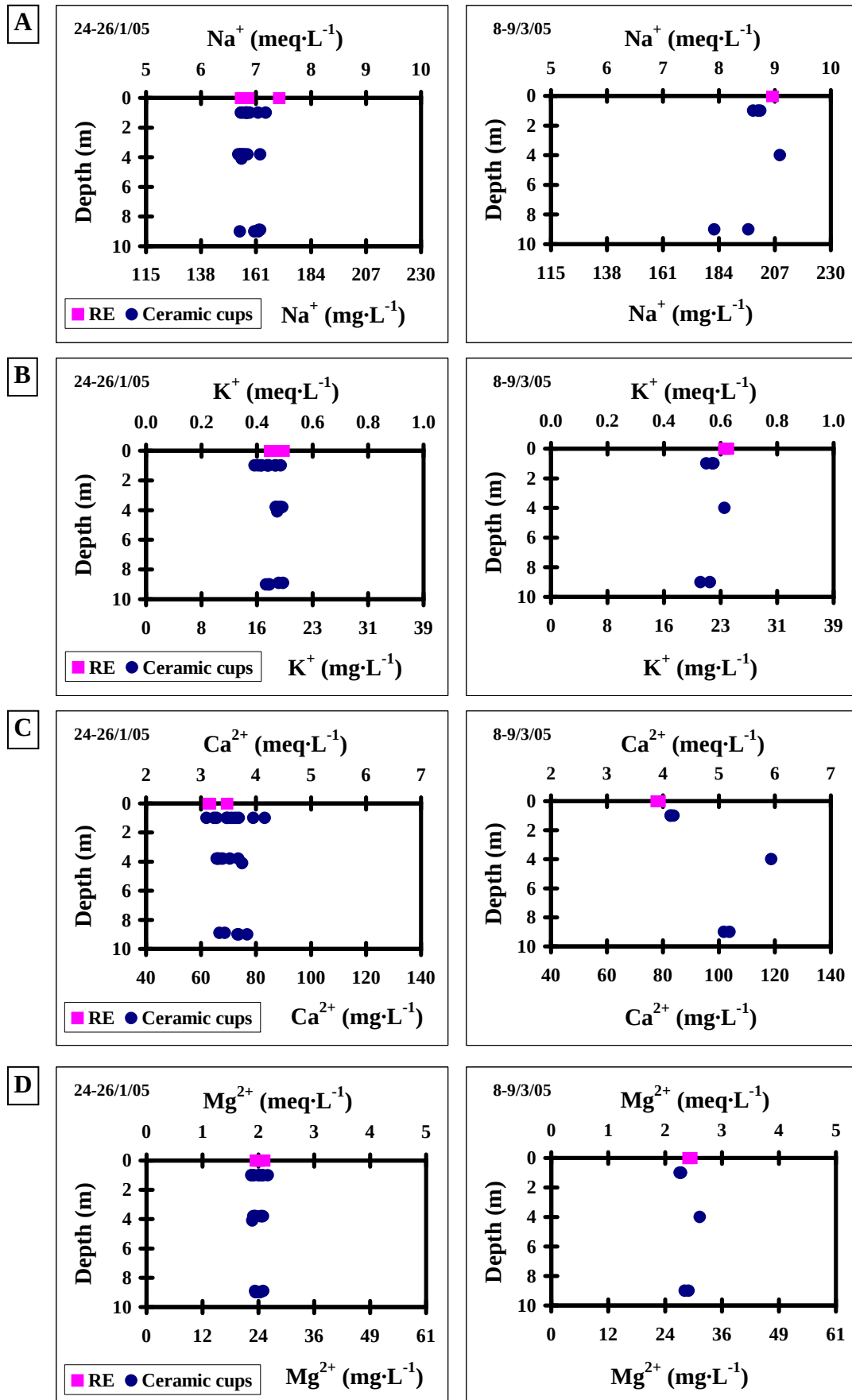


FIGURE 3.10: Concentrations of (A) Na^+ ; (B) K^+ ; (C) Ca^{2+} ; and (D) Mg^{2+} in the RE and in the infiltrating effluents in the upper 9 m of the vadose zone below the basin, sampled from ceramic cups during two sampling campaigns.

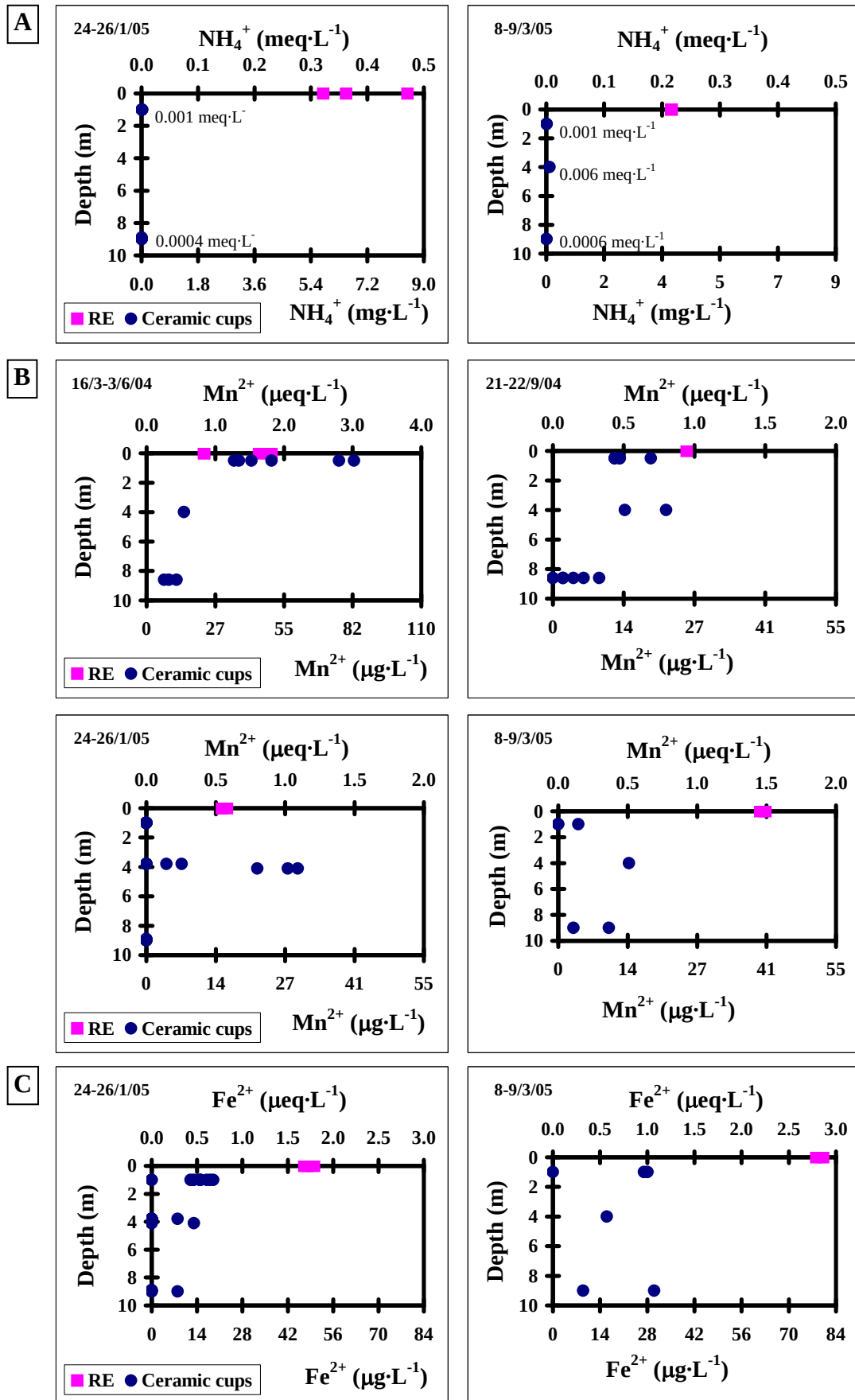


FIGURE 3.11: Concentrations of (A) NH_4^+ ; (B) Mn^{2+} ; and (C) Fe^{2+} in the RE and in the infiltrating effluents in the upper 9 m of the vadose zone below the basin, sampled from ceramic cups during two sampling campaigns. For Mn^{2+} four sampling campaigns are presented. Zero values of Mn^{2+} and Fe^{2+} indicate concentrations $< 0.2 \mu\text{eq}\cdot\text{L}^{-1}$.

Chapter 4

Manganese in the sedimentary column of the aquifer

4.1 Introduction

The manganese inventory, its distribution and "fingerprints" for its mobilization in the sedimentary column of the aquifer were studied in three wells. The wells were located at different distances from the Yavne-2 infiltration basin (Fig. 4.1). One well (T/283) was drilled in the center of the infiltration basin. At this site, the infiltrating effluents have been flowing along the 40 m vadose zone for the past 20 years. The well was drilled to a depth of 80 meters, i.e. 40 m below the water table, allowing sampling of sediments from both the vadose and the saturated zone, just below the infiltration basin. The second well (T/284) was drilled 200 m from the basin, near a production well that pumps 100% effluents with **high** manganese concentrations, while the third well (T/285) was drilled 560 m from the basin, near a production well that pumps 100% effluents with **low** manganese concentrations. The vadose zone in both T/284 and T/285 was not in contact with effluents from the SAT system and therefore the sediments collected from this zone were considered as representing the pristine sediments overlaying the Coastal Aquifer.

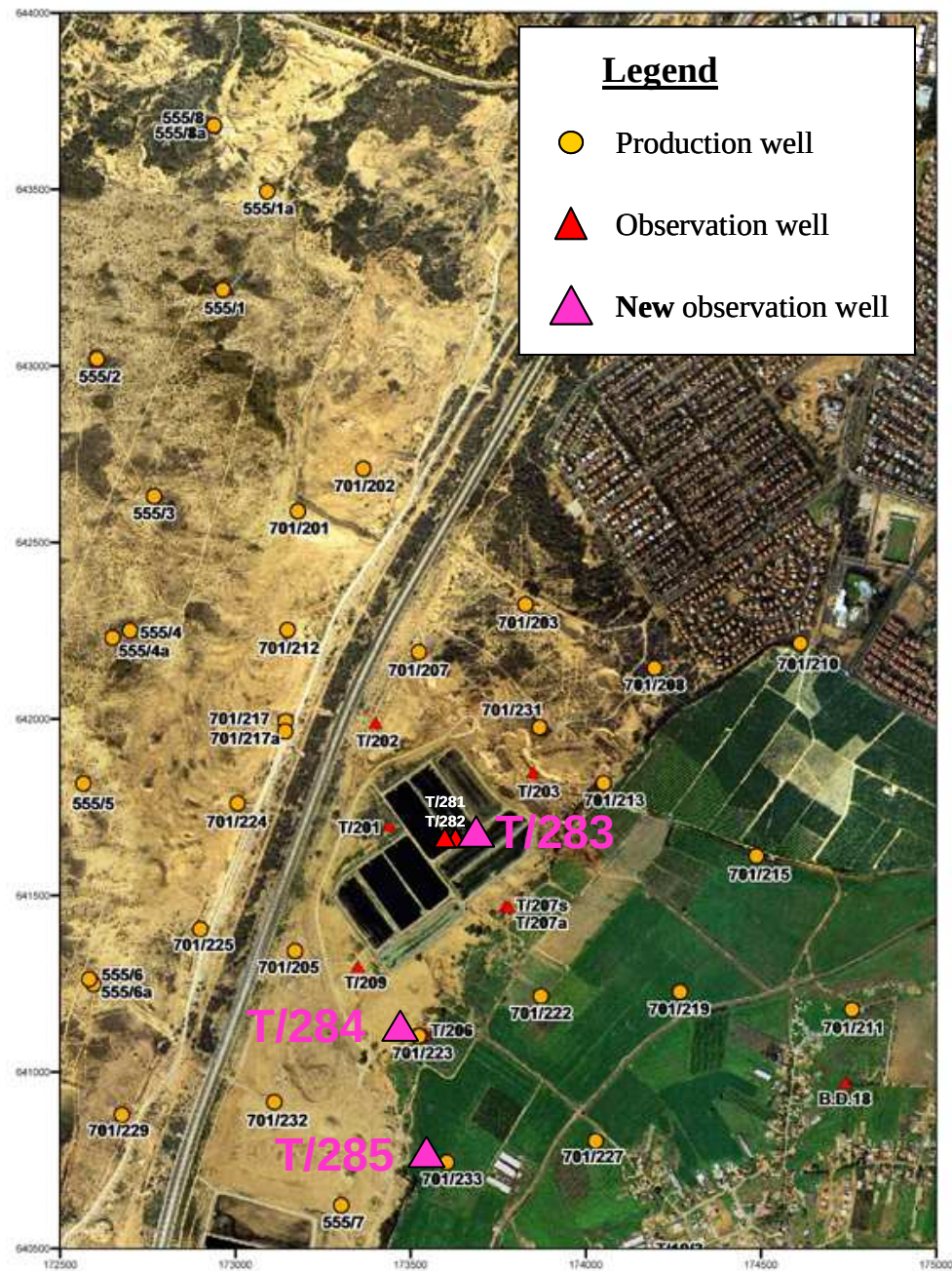


FIGURE 4.1: Location map of the three wells that were drilled in order to sample the sediment profiles in the SAT system: well T/283, 80 m deep in the center of the Yavne-2 infiltration basin; well T/284, 80 m deep and 200 m from the basin; well T/285, 60 m deep and 560 m from the basin.

4.2 Methods

4.2.1 Drilling the wells

Drilling was carried out with a dual system drilling instrument. In this drilling method the casing tubes are lowered simultaneously with the drill bit while the sediment cuttings are normally removed from the borehole by compressed air. This method enables drilling with no addition of drilling mud or water. Uncontaminated sediment and water samples from different depths can thus be collected during the drilling. In a few cases, local water (collected earlier from the borehole itself or from an adjacent well) had to be introduced into the borehole during the drilling to prevent the rise of unconsolidated sands through the casing tubes. The drilling diameter was 6-8" (15-20 cm). At the end of the drillings, the wells were fitted with 2" (5.1 cm) diameter PVC tubes that were perforated at the depth ranges of 70-80 m, 25-40 m and 33-60 m, in T/283, T/284 and T/285 respectively (Figs. 4.2 - 4.4). The annular space around the perforations was packed with pre-washed quartz gravel and the space above was filled with local material removed from the boreholes during the drilling.

4.2.2 Sediment sampling and treatment

The sediment profiles were sampled during the drilling to obtain the following:

- *Lithological description* - samples were collected every 3 m into archive boxes that were used later to draw the appropriate sections (Figs. 4.2 - 4.4).
- *Chemical analyses* - sediment samples were collected every 1.5 m (the size of the drilling rods) into 50 mL vials, frozen on site with dry ice and transferred to the laboratory within 12 hours. In the laboratory the samples were freeze-dried and crushed manually to obtain homogenous samples.
- *Clay content* - about 0.5 kg of sediment samples were collected every 3 m into plastic bags.

4.2.3 Sediment analyses of clay and carbonate contents and Mn concentrations

The clay fraction ($<2\ \mu\text{m}$) in few representative samples of the different kinds of sediments was determined by the sedimentation method, following [Black, 1965](#).

The CaCO_3 content in the sediments was determined in the following way: 1-3 g of crushed sample was put into a constant volume sealed canister ("bomb") equipped with a pressure gauge, into which 1:5 HNO_3 acid was added. A calibration curve was prepared by introducing different amounts of pure CaCO_3 into the bomb that produced different CO_2 pressures correlated to the CaCO_3 content.

Total Mn concentration in the sediments was determined by the sintering method, following [Ilani et al., 1992](#): 500 mg of the sample was mixed with 2 g Na_2O_2 in a zirconium crucible and heated in a muffle furnace at 500°C for 40 minutes. After some cooling in open air, the crucible with the sintered mass was placed in a plastic beaker filled with distilled water. 20 mL HNO_3 (5 M) were then immediately added to the crucible and the mixture was mixed on a magnet stirrer until dissolution was completed. The solution was then transferred to a volumetric flask (100 mL) to which Sc solution was added to yield 5 ppm (as an internal standard). The chemical analyses were carried out on a Perkin Elmer Optima 3300 ICP-AES.

In order to distinguish between the different forms of Mn present in the sediments, sequential extraction was carried out on selective samples. Sequential extraction procedures were developed through numerous studies which attempted to improve the method, including for specific elements (e.g., [Tessier et al., 1979](#); [Davidson et al., 1998](#); [Ma and Uren, 1998](#); [Sutherland and Tack, 2002](#); [Mossop and Davidson, 2003](#); [Neaman et al., 2004](#)). Generally, sequential extraction is based both on the solubility of the different solid phases and the selectivity and specificity of the chemical reagents ([Han et al., 2001](#)). Therefore, the procedure provides a physicochemical reactivity gradient and does not allow full distinction between the different forms of an element ([Martin et al., 1987](#)).

The procedure employed in this study was modified after [Han and Banin, 1995](#). . This procedure was adapted to the high-carbonate soils of Israel and was widely used in soil studies in Israel ([Han and Banin, 1997](#); [Han et al., 2001, 2003](#); [Teutsch et al., 2001](#)), including in the Shafdan SAT system ([Banin and Lin, 2003](#); [Lin et al., 2004](#)).

In the present study the aim was to distinguish between the following Mn forms: soluble and exchangeable Mn, Mn in carbonates, easily-reducible Mn oxides, and Mn bound to organic matter. Accordingly, the procedure comprised four steps (Table 4.1):

Step 1 - soluble and exchangeable Mn: 1 g of dried sediment is shaken in 40 mL NH_4NO_3 solution for 30 minutes. The mixture is then centrifuged and the supernatant decanted and analyzed following the procedure described above for the analyses of the sintered samples. Duplicate extractions and analyses of few representative samples indicate that the reproducibility of the extractions is within 10%.

Step 2 - Mn in carbonates: 40 mL sodium-acetate solution is added to the residue from step 1 and shaken for 1 hour. The supernatant is then decanted and analyzed as described above.

Step 3 - easily-reducible Mn oxides: 40 mL hydroxylamine-hydrochloride solution is added to the residue from step 2 and shaken for 30 minutes. The supernatant is then decanted and analyzed.

Step 4 - Mn bound to organic matter: 40 mL hydrogen-peroxide solution is added to the residue from step 3 and shaken in a water bath at 80°C for 3 hours. The supernatant is then decanted and analyzed.

TABLE 4.1: Sequential extraction procedure for 1 g of sediment sample, modified after Han and Banin, 1995. A solution/sediment ratio of 40:1 was maintained in all steps.

Step No.	Targeted fractions	Sediment weight	Solution	Concentration	pH	Solution volume	Shaking time	Temp
1	soluble and exchangeable Mn	1 g	NH_4NO_3	1 M	7	40 ml	30 min	room temp
2	Mn bound to carbonates	1 g	NaAc	1 M	5	40 ml	1 h	room temp
3	easily-reducible Mn oxides	1 g	$\text{NH}_2\text{OH}\cdot\text{HCl}$	0.5 M	2.5	40 ml	30 min	room temp
4	Mn bound to organic matter	1 g	H_2O_2	30%	2.6	40 ml	3 h	80°C

The chemical analyses of all solutions from the above procedures were carried out on a Perkin Elmer Optima 3300 ICP-AES. Duplicate extractions and analyses of few representative samples indicate that the reproducibility of the system is within 10%.

4.3 Lithologic description

The sedimentary column in the three wells comprises mainly calcareous sandstone and sand in varying proportions (Figs. 4.2 - 4.4). The clay ($< 2 \mu\text{m}$) content of these calcareous sandstones was found to be less than 3% and commonly less than 1%. The few clayey layers identified in the field were found mainly in the upper part of the section, above the water table. Sedimentary analyses indicate that the clay content in these horizons vary between 7 and 24% (Table 4.2). The Carbonate content varied between 7% and 15% in the calcareous sandstone and about 2% in the clayey sediments, except a sandy marlstone sample that contains 24%.

TABLE 4.2: Clay ($< 2 \mu\text{m}$) and Carbonate contents in several representative samples from the wells.

Sample	Lithological field description	Clay content %	Carbonate content %
T/283, 68.5-71.5 m	Calcareous sandstone	< 1	8
T/284, 8.5-11.5 m	Fine-grained sand, yellowish	1	10
T/284, 29.5-32.5 m	Calcareous sandstone + sand	< 1	7
T/284, 38.5-41.5 m	Calcareous sandstone + sand	< 1	7
T/284, 59.5-62.5 m	Calcareous sandstone + sand	3	15
T/284, 2.5-5.5 m	Clayey-marly sand, brown-red	13	1.5
T/284, 71-71.5 m	Sandy marlstone, gray	24	24
T/285, 15.7-17.5 m	Clayey-marly sand, brown-black	7	2.2
T/285, 29.5-32.5 m	Clayey-marly sand, brown	19	2.5

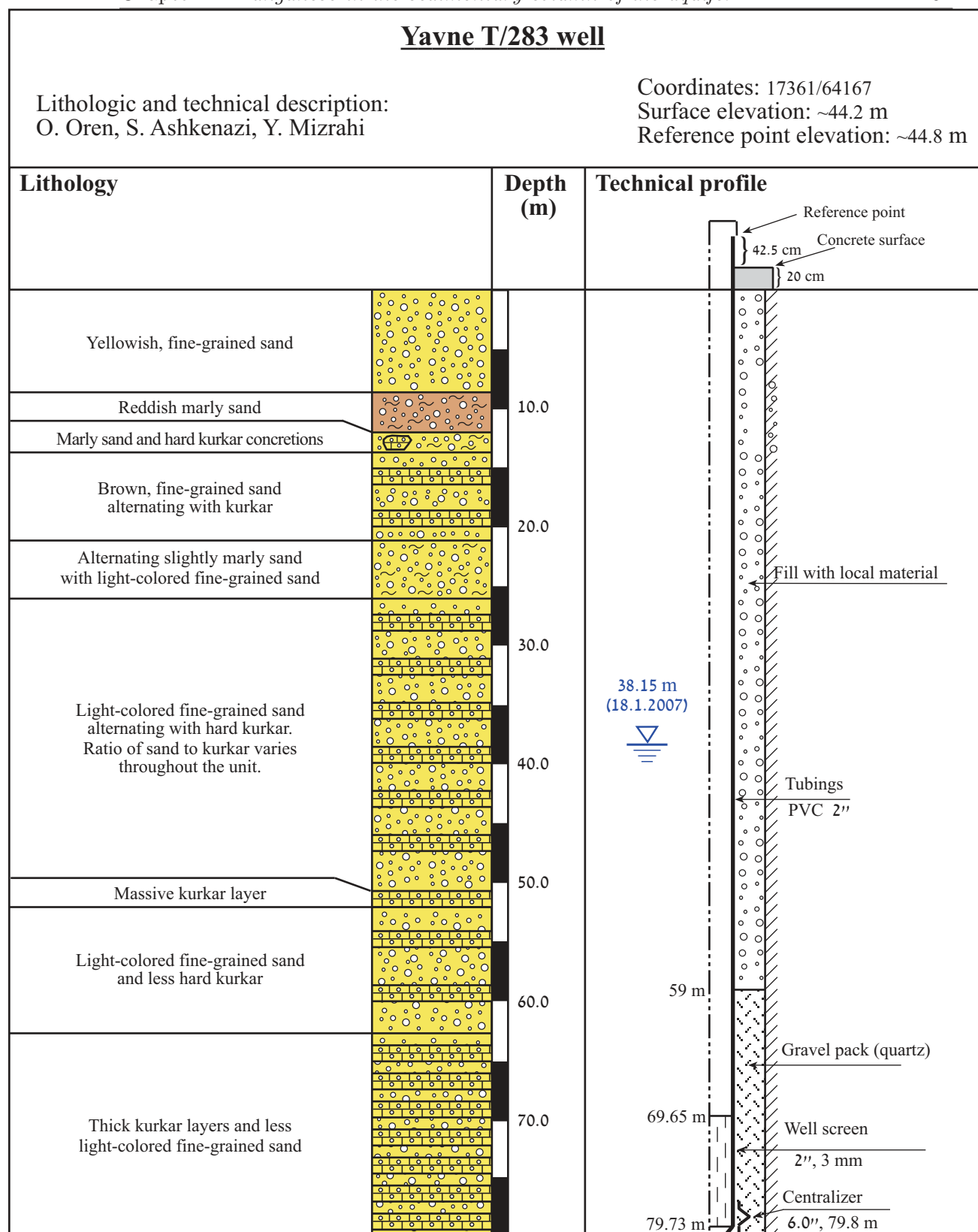


FIGURE 4.2: Lithologic and technical profile of Yavne T/283 observation well. The yellow layers are permeable whereas the brown are impermeable in nature.

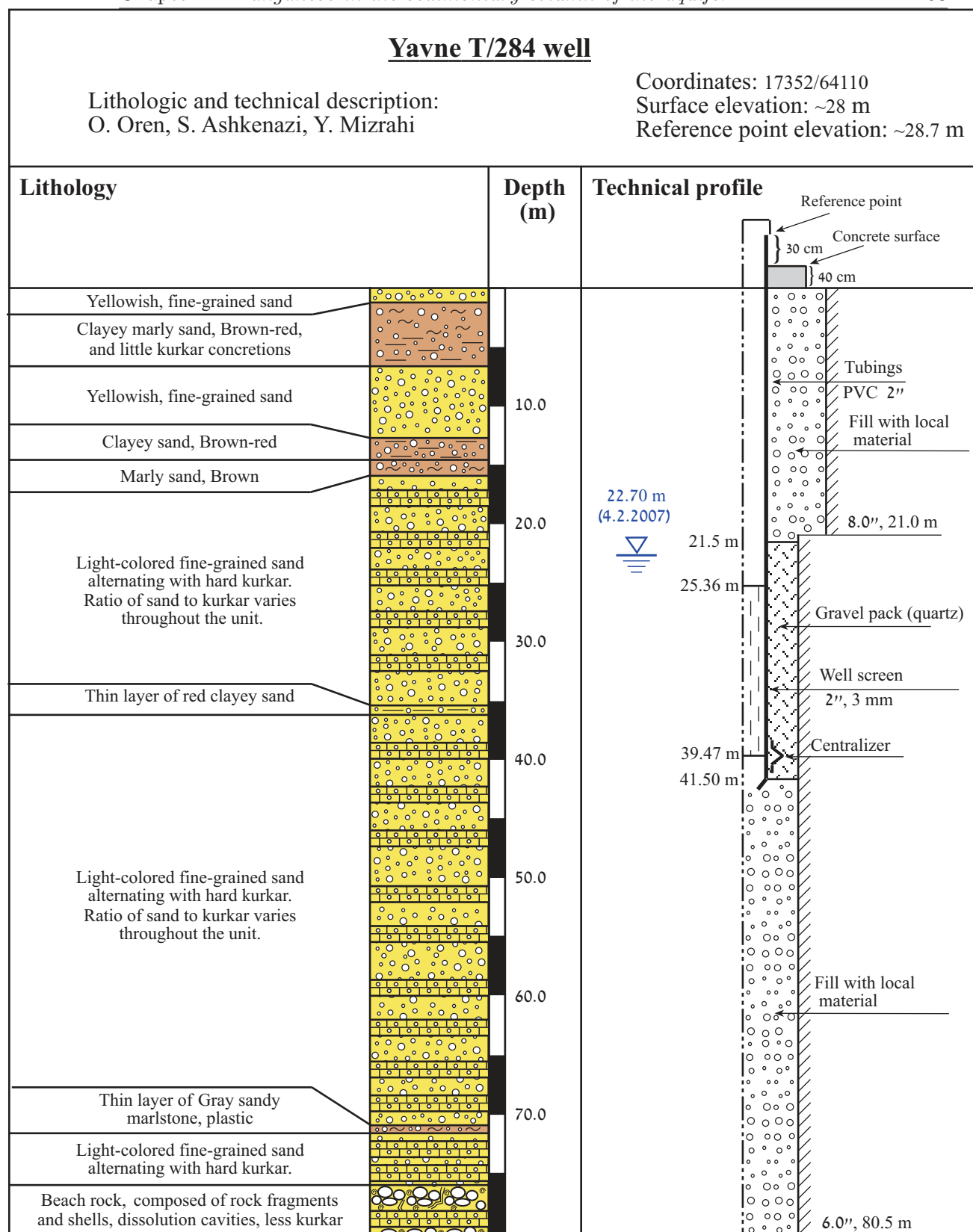


FIGURE 4.3: Lithologic and technical profile of Yavne T/284 observation well. The yellow layers are permeable whereas the brown are impermeable in nature.

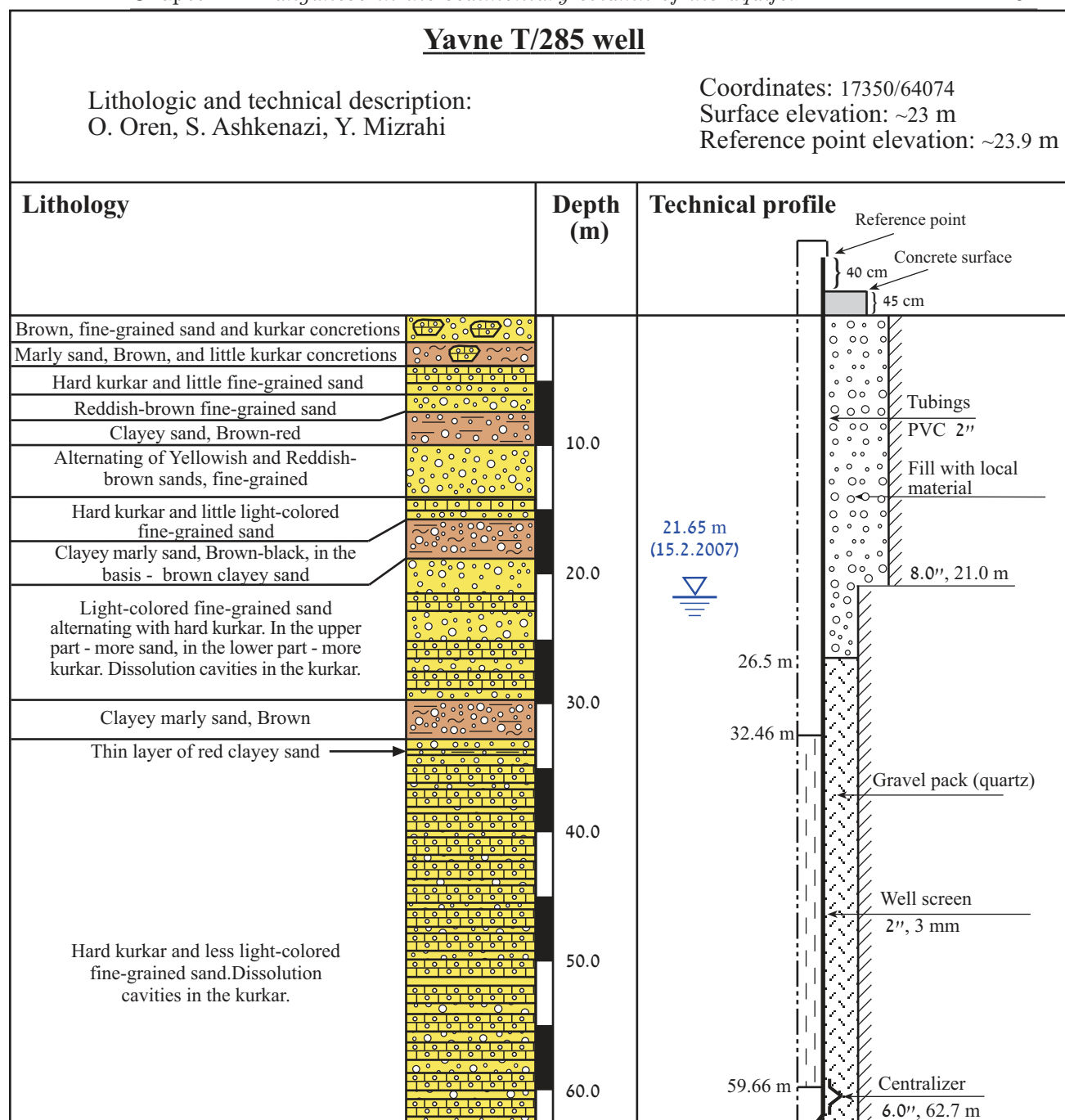


FIGURE 4.4: Lithologic and technical profile of Yavne T/285 observation well. The yellow layers are permeable whereas the brown are impermeable in nature.

4.4 Manganese content and its distribution

4.4.1 Total manganese content

The total Mn content in the sediments, above and below the water table, varies from 30 to 480 mg·kg⁻¹ (Fig. 4.5). In general, the total Mn content in the clayey sediments (300-480 mg·kg⁻¹) is much higher than that in the calcareous sandstone sediments (30-220 mg·kg⁻¹). However, only two thin clayey layers were identified below the water table (one in T/284 and the other in T/285); in both, the total Mn content was found to be similar to that in the pristine clayey layers (above the water table) (Fig. 4.5). In fact, these two layers are clearly insufficient to represent the Mn inventory and behavior in the clayey sediments in the entire aquifer. The limited spatial extension of local clayey horizons in the aquifer and the difficulty to identify them during the drilling make the estimation of their real significance impractical.

The total Mn content in the pristine calcareous sandstone (from the vadose zones of T/284 and T/285) ranged between 100 and 220 mg·kg⁻¹. In the aquifer (below the water table) the total Mn contents in the calcareous sandstone varied between similar to lower values. The lower Mn content of 30-~50 mg·kg⁻¹ indicates that it was leached from the sediments, probably due to reductive dissolution of Mn-oxides. The variability in the Mn content along the aquifer profiles suggests significant spatial differences in the intensity of the mobilization processes. Mass balance of Mn in the aquifer cannot be calculated based on these results, but on the **dissolved** Mn concentrations, which better averages the processes that take place in the aquifer (see Chapter 5).

4.4.2 The distribution of the various Mn forms

The distribution of four different forms of Mn was evaluated by the four-step sequential extraction. However, the results suggest that part of the adsorbed Mn was not leached in the first leaching step (which is supposed to extract the exchangeable Mn) but only in the second one (which is supposed to extract the carbonate Mn). Assuming that the content of Mn in carbonates is proportional to the carbonate content in the sediment, the concentrations of this form should be much higher in the calcareous sandstone than in the clayey sediments. Also, due to the high CEC in clays, the adsorbed Mn form should

be present in greater concentrations in the clayey sediments. Yet, such correlations were not found (Appendix 7). The above two observations imply that a substantial amount of the adsorbed Mn is not exchangeable. Accordingly, in the present study the results of the first two Mn leaching steps were combined. Thus, the Mn in the sedimentary column was divided into three Mn forms: adsorbed + carbonate Mn, easily-reducible Mn oxide, and Mn bound to organic matter (Fig. 4.6).

The total amount of Mn leached by the 4-step sequential extraction was in the range of 215-380 mg·kg⁻¹ in the clayey sediments and 15-200 mg·kg⁻¹ in the calcareous sandstone sediments. These values were always lower than the total Mn derived for the same sediment by sintering. The "missing" Mn, unretrieved in the sequential extraction varies from 15% to 80% of the total Mn as determined by sintering. The "missing" Mn is generally lower in the clayey sediments as compared to the calcareous sandstones (averages of 28% and 48%, respectively). The unretrieved fraction probably represents the Mn bound within the soil's minerals or the non-easily-reducible oxides (Banin and Lin, 2003).

Most of the Mn extracted by the sequential extraction was found to be in the form of Mn oxides (Figs. 4.6, 4.7). The Mn oxide content in the pristine clayey sediments varied between 150 and 330 mg·kg⁻¹, whereas in the pristine calcareous sandstone it varied between 50 and 130 mg·kg⁻¹. The adsorbed + carbonate Mn in both the clayey sediments and calcareous sandstone is relatively small (Fig. 4.7), generally varying in the range of 2-30 mg·kg⁻¹, unrelated to any identifiable parameter (e.g. clay content, pristine vs. disturbed, depth etc.). Therefore, this range is attributed to the natural variation of the sediments. The Mn content in the organic matter is also small (Figs. 4.6, 4.7), but is significantly higher in the clayey layers (20-40 mg·kg⁻¹) than in the calcareous sandstone (≤ 10 mg·kg⁻¹). No enrichment of organic bound-Mn was found in the sediments that are impacted by the SAT operation.

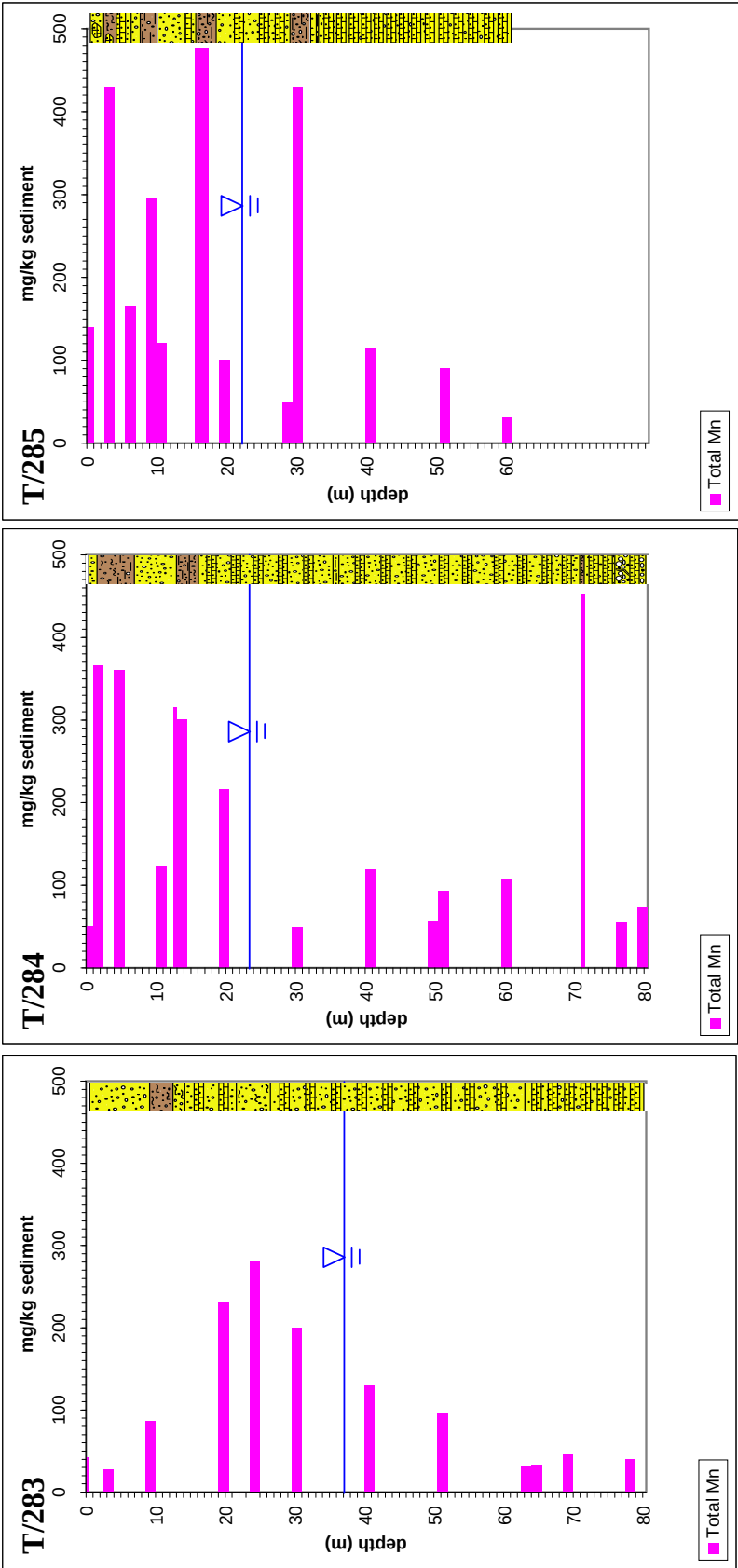


FIGURE 4.5: Total Mn content in the sediments sampled from the three research wells. The geological section of each well is given on the right end of the graphs and their description is given in Figs. 4.2, 4.3 and 4.4.

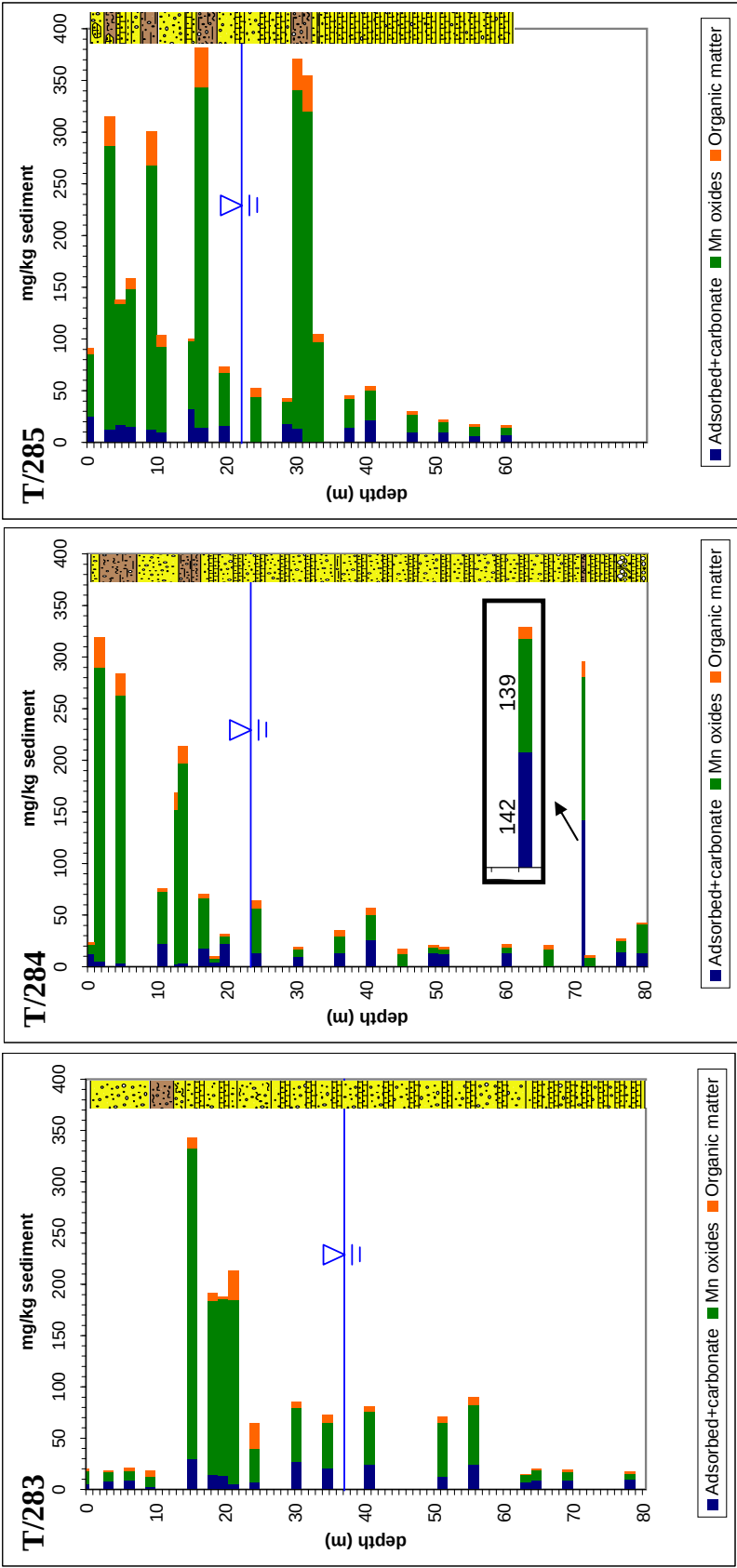


FIGURE 4.6: The distribution of the various Mn forms as determined by sequential extraction of the sediments in the three research wells. The geological section of each well is given on the right end of the graphs and their description is given in Figs. 4.2, 4.3 and 4.4.

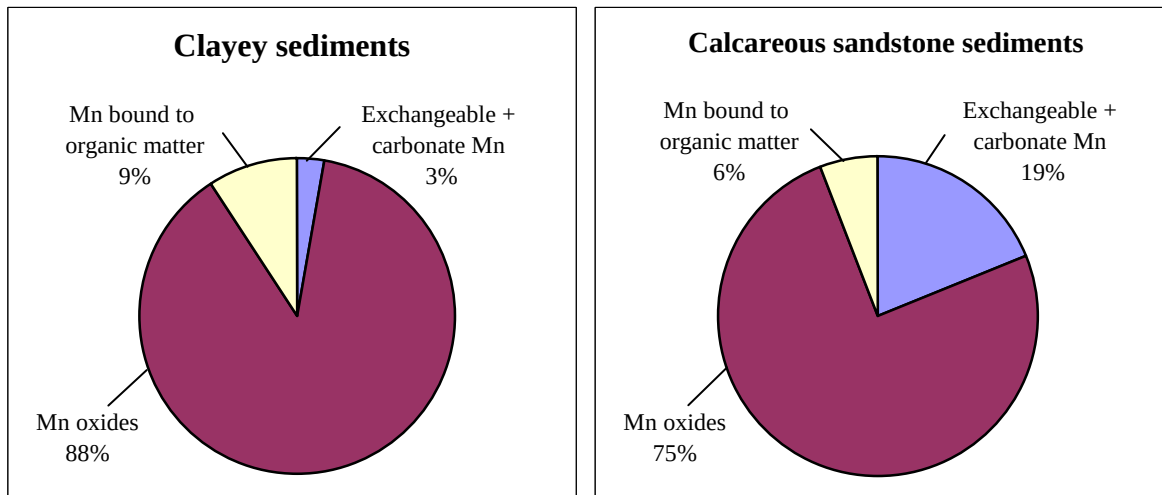


FIGURE 4.7: The relative distribution of Mn forms in the pristine clayey sediments and calcareous sandstone sediments forming the vadose zone above the aquifer (average values).

The sediments in the vadose zone of well T/283 were affected by the infiltrating effluents. The low Mn content along the upper 10 m (Fig. 4.6) suggests that the Mn oxides were removed from the sediments, probably through reductive dissolution and mobilization. A similar decline in Mn-oxides was observed by Banin and Lin, 2003 in the Soreq infiltration basin of the Shafdan. Below 10 m, Mn oxide content was found to be higher than the natural background, indicating re-oxidation and precipitation of the dissolved Mn that was leached from the upper parts. These observations show that dissolution-precipitation (through reduction-oxidation) controls the Mn mobilization within the vadose zone. Between 23 and 57 m depth, the Mn content was found to be similar to that of the pristine sediment, with no difference between the sediments above and below the water table of the aquifer (37 m, Fig. 4.6). Below 60 m, the low Mn oxides content (along with low total Mn content) indicates reduction and mobilization of Mn within the deeper part of the aquifer. This implies that the redox conditions that enhance Mn-oxides reduction are established at this depth, and apparently do not develop in the upper part of the aquifer below the infiltration basin.

In well T/284, the calcareous sandstone, which forms most of the sedimentary column below the water table, is characterized by a low Mn-oxides content relative to the pristine calcareous sandstone sediments. This indicates that along the entire profile of the aquifer in this area, Mn was reduced and mobilized. This correlates well with the high concentration of dissolved Mn^{2+} in the groundwater recovered from this well (Appendix

3) and from the adjacent production well (well 223; Appendices 1,2). Evidence for this process was found in the thin clayey layer at the depth of 71 m (Fig. 4.6). While the total Mn content in this layer remains high and similar to that in the pristine clayey layers, the distribution between its Mn forms is significantly different. Here, the Mn oxide content is about half that in the pristine clayey layers, and is compensated by an equivalent increase in the adsorbed + carbonate Mn. This observation implies that the Mn oxides in the clayey layers were reduced and immediately adsorbed onto the clays. It also emphasizes the importance of the clayey layers as the main source of Mn oxides and the main sink of the adsorbed Mn, as well as their overall role in Mn mobilization.

[Banin and Lin, 2003](#) also reported a decrease in the fraction of Mn oxide and an increase in the exchangeable + carbonate Mn fractions in calcareous sandstone sediments below the water table under the Soreq infiltration basin. They attributed these observations to the reduction of Mn from IV/III valences to a II valence, in accord with the reductive conditions that prevailed under the water table level. The present findings agree well with their observations and explanation.

Well T/285 has the lower dissolved Mn^{2+} concentration and is located downstream relative to well T/284. A clayey layer some 10 m below the water table has Mn forms content and distribution similar to that in the pristine clayey layers above, in the vadose zone (Fig. 4.6). This suggests that the processes that govern Mn mobilization, namely Mn-oxide reduction and Mn^{2+} adsorption, are less intensive in this area of the aquifer. Nevertheless, low Mn-oxides and total Mn contents in calcareous sandstone sediments in the lower part of this well (below depth of 45 m) indicate that these processes do take place in depth at such a distance from the infiltration basin.

4.5 Summary

The main Mn form among the easily extractable forms in the sediments of the Yavne-2 SAT system is Mn oxide. The fractions of adsorbed + carbonate Mn and the organic matter Mn are minor.

Low total Mn content and Mn-oxides in the calcareous sandstone sediments of the aquifer, below the water table, relative to that of the pristine sediments point to reduction and mobilization of Mn within the saturated zone of the aquifer. Decrease in

the Mn oxide content and equivalent increase in the adsorbed + carbonate Mn in a clayey layer in well T/284 may indicate adsorption of reduced Mn^{2+} , which occur immediately upon the reduction of the Mn-oxides in this layer.

The Mn content in the clayey layers is much higher than that in the calcareous sandstone. The Mn content in the pristine sediments varies between 300 and 480 $\text{mg}\cdot\text{kg}^{-1}$ in the clayey sediments and between 100 and 220 $\text{mg}\cdot\text{kg}^{-1}$ in the calcareous sandstones. This emphasizes the role of the clayey layers in controlling the behavior of the Mn system in a sandy aquifer. It is impossible to quantify the effect of the clayey layers on the Mn system from the three wells drilled for this study because these layers are hard to identify during drilling and their spatial distribution is very low. Larger number of research wells would probably help in resolving this problem. It is concluded that the analyses of the sediments from the wells provided valuable information on the main processes occurring in the subsurface of the SAT system, but cannot be used for reconstruction of a Mn mass balance for the aquifer. The data on the dissolved Mn however was used to calculate a reliable mass balance (see Chapter 5) because the water flowing through the aquifer averages a large portion of the sedimentary section.

Chapter 5

Manganese mobilization and enrichment during soil aquifer treatment (SAT) of effluents, the Dan region sewage reclamation project (Shafdan), Israel

Manganese Mobilization and Enrichment during Soil Aquifer Treatment (SAT) of Effluents, the Dan Region Sewage Reclamation Project (Shafdan), Israel

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The composition of groundwater reclaimed from tertiary soil aquifer treatment systems reflects the dynamic processes taking place in the subsurface, between the infiltration basin and the production wells. At the end of year 2000, following more than a decade of operation, high Mn concentrations ($2 \mu\text{mol L}^{-1} \leq \text{Mn} \leq 40 \mu\text{mol L}^{-1}$) appeared in the reclaimed effluents of the Dan Region Sewage Reclamation Project (Shafdan), Israel. A mass balance indicates that the high Mn excess originated from the aquifer rocks, most likely following reduction of sedimentary Mn-oxides under suboxic conditions. The subsequent adsorption of the Mn^{2+} results in a slow Mn^{2+} front that advances in the direction of groundwater flow only when all the Mn^{2+} exchangeable sites are saturated. A retardation factor obtained from two independent estimates based on a simple reduction–adsorption–advection model yields a value of about 10. This explains the delayed appearance of the high Mn concentrations at a distance of only ~500 m from the infiltration basin.

Introduction

Soil aquifer treatment (SAT) is commonly considered an efficient tertiary treatment process of effluent water. The effluents are purified by physical, chemical, and biological processes in the vadose zone and in the aquifer that remove essentially all biodegradable organics, suspended solids, bacteria, and viruses from the wastewater, and almost all the phosphorus and heavy metals (1). The advantages of the SAT system include large throughput volumes of effluents, use of the recharging aquifer as an underground reservoir, high quality of the reclaimed effluents, simplicity of operation, low operational costs, and the reliability of the system (1, 2).

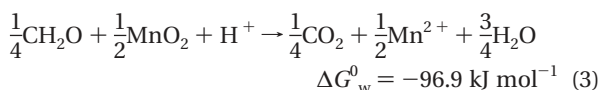
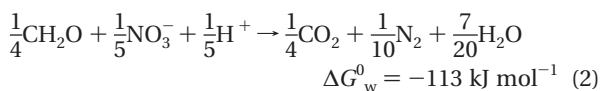
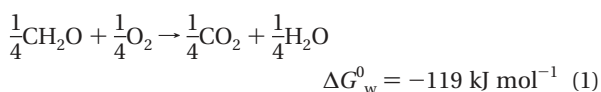
The Dan Region Sewage Reclamation Project (Shafdan) is one of the pioneers around the world to use SAT. The plant treats much of the municipal wastewater of the Tel Aviv metropolitan area, which is the most densely populated region in Israel. Since onset of operation in 1977, the facility has treated and recharged about 1700 million cubic meter

(MCM) of effluents and presently reclaims some 110–130 MCM annually. Following filtration and secondary treatment by activated sludge, the effluents are recharged into the aquifer for their SAT tertiary treatment and are subsequently recovered by a series of production wells (3, 4). By the time the effluents are reclaimed in these production wells, their quality has greatly improved and they are qualified for unrestricted irrigation and incidental drinking.

A severe degradation in the quality of the reclaimed effluents was observed after about 25 years of operation, at the end of 2000, when high Mn concentration ($2 \mu\text{mol L}^{-1} \leq \text{Mn} \leq 40 \mu\text{mol L}^{-1}$) appeared in the production wells. Since then Mn concentrations in fourteen of the production wells have been much higher than those in the recharged effluents (about $0.6 \mu\text{mol L}^{-1}$) and the Israeli recommended maximum concentration level for irrigation with effluents ($3.6 \mu\text{mol L}^{-1}$). This suggests that Mn is mobilized within the SAT system, most probably due to reduction of Mn-oxides. Indeed, reductive dissolution of Mn-oxides coupled with oxidation of organic matter (OM) reactions was previously suggested as the mechanism responsible for substantial Mn loss from the upper 4 m of the vadose zone below one of the infiltration basins in the Shafdan (5). The increase in dissolved Mn caused serious operational problems such as precipitation of Mn-oxides in the main pipeline supplying reclaimed effluents to southern Israel and clogging of drippers in agricultural irrigation systems.

The objectives of this study are to examine the biogeochemical processes that are responsible for the Mn mobilization in the SAT system of the Shafdan plant and to account for the sudden rise in Mn concentration in the reclaimed effluents.

Redox Behavior of Mn in Groundwater. Mn mobilization by groundwater is controlled mainly by redox reactions. In aerobic environments, Mn oxides such as MnO_2 and MnOOH are highly insoluble, whereas under suboxic conditions, Mn oxides are reduced to the much more soluble Mn^{2+} species and become readily mobilized in the aquifer. According to the redox potential sequence, $\text{Mn}^{3+},^{4+}$ will act as electron acceptor during OM oxidation once most of the oxygen and nitrate have been consumed (6). This follows the decrease in the free energies of the following OM (represented here as CH_2O) oxidation reactions (7):



Despite the difference in their free energies, simultaneous reduction of nitrate and Mn-oxides is common in low oxygen (subaerobic) environments (8, 9). Hence, groundwater with initial high load of OM and low dissolved oxygen (DO) flowing in aquifers containing Mn-oxides phases may reduce these oxides and accumulate substantial amounts of dissolved Mn^{2+} . Examples for Mn mobilization in groundwater under subaerobic conditions include river bank-filtration systems (9–12) and landfill-leachate polluted aquifers (8). These

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and the surrounding freshwater, thereby minimizing leakage into the main body of the Coastal Plain aquifer. The residence time of effluents in the aquifer is about 1 year. The reclaimed effluents are then piped for irrigation to the Negev desert in southern Israel.

The thickness of the vadose zone below the infiltration basins is 30–40 m. The recharged effluents form a high groundwater mound beneath each infiltration basin which is several meters above the regional water level (Figure 1, Figure SI-1). The Yavne-2 infiltration basin recharges 18–30 MCM of effluents annually, which is equivalent to 100–170 m y^{-1} , significantly more than the local recharge from winter precipitation (0.5 m y^{-1}). Generally, the annual volume of reclaimed effluents from the Yavne-2 plant is similar to the volume of effluents recharged through its infiltration basin, with some seasonal and inter-annual variations. Since its inauguration in 1988, the Yavne-2 infiltration basin treated some 450 MCM.

Materials and Methods

Water Sampling from the Vadose Zone. Effluents after secondary treatment were sampled directly from the infiltration basin. The infiltrating effluents in the vadose zone below the basin were sampled by ceramic cups (14, 15) installed at various depths between 0.5 and 9 m. Water from the cups was pumped by a peristaltic pump directly to 100 mL syringes from which the water was taken for different analyses. The cups were installed in narrow holes, dry-drilled with a 3 inch diameter spiral drill bit. After installation, the holes were refilled with the original sandy sediments. Water sampling was carried out at least 3 weeks after installation (several flooding cycles), in order to allow the surroundings of the cups and the overlying sediments to return to their original settings.

Several shallow perched horizons were encountered beneath the infiltration basin during the drilling. In order to sample the perched water, a 2 inch PVC pipe monitoring well was installed to a perched horizon at 7 m depth (observation well YAV-21 in Figure 1). Drilling and installation of the well were identical to the installation of the ceramic cups. The well was sampled twice for chemical analyses and the depth of the water table was measured several times during the study period.

Water Sampling from the Aquifer. Historical data on the volumes of recharged effluents and reclaimed effluents and their chemical compositions were provided by Mekorot Water Co.. Generally, the charge imbalance of the historical chemical data is less than 2%.

All observation and production wells around the Yavne-2 infiltration basin were sampled annually during 2004 and 2005. Samples for trace element analyses were filtered (0.45 μm) in the field and acidified with HNO_3 . Samples for Kjeldahl-nitrogen (NKJT; organic N + NH_4^+) and dissolved organic carbon (DOC) were acidified with H_2SO_4 and HCl, respectively. Samples for dissolved inorganic carbon (DIC) were collected in brown glass bottles and immediately poisoned with HgCl_2 . Standard Winkler reagents were added to samples collected for DO determination.

Two observation wells were drilled in the center of the Yavne-2 infiltration basin: well T/281, 50 m deep (10 m below water table); and well T/282, 60 m deep (20 m below water table). Drilling was conducted using a rotary drill with drilling mud, and the wells were fitted with 2 inch diameter PVC tubes that were perforated in the depth ranges of 38–47 m and 48–59 m, respectively. The annular space around the perforations was packed with quartz gravel. The wells were treated with polyphosphate to remove the drilling mud and were then pumped until the water was clear and phosphate concentrations dropped to background concentration. The wells were then left to equilibrate with the regional ground-

water for at least 1 month before sampling. Based on recharge rates, this period corresponds to the time required to replace all the groundwater in the vicinity of the wells with fresh recharged effluents. To further ensure representative groundwater sampling, the equivalent of 3 times the water volume present within each well was pumped prior to sampling (16). Pumping was done with a submersible pump to avoid oxidation of the water.

Chemical Analyses. Most of the chemical analyses were carried out in the laboratories of the Geological Survey of Israel. Major cations, Mn and Fe, were analyzed on a Perkin-Elmer Optima 3300 ICP AES. Anion concentrations were measured using a Dionex ICS-2000 ion chromatograph. Alkalinity (ALK) was determined by titration with 0.02N HCl. DIC was determined using two methods: (1) Collection and measurement of CO_2 obtained in a vacuum line by adding 1 mL of H_3PO_4 to about 50 mL of the water sample. (2) Analyses on a ThermoFinnigan Delta Plus XP mass spectrometer connected to a Gas Bench II interface (17). The analytical precision of these methods is better than 0.1 mmol L^{-1} . DO was measured several times in the field with a gold electrode but commonly it was determined in the laboratory following the Winkler titration method. Ammonium (NH_4^+) was measured on a Turner Designs Aquafluor after Holmes et al. (18). DOC and NKJT were measured at the Nesin laboratory of Mekorot Water Co. following the Standard Methods (19). The analytical precisions of DOC analyses are 20 $\mu\text{mol L}^{-1}$ for concentrations higher than 1000 $\mu\text{mol L}^{-1}$ and 10 $\mu\text{mol L}^{-1}$ for lower concentrations; the precisions of NKJT analyses are 15 $\mu\text{mol L}^{-1}$ for concentrations higher than 100 $\mu\text{mol L}^{-1}$ and 5 $\mu\text{mol L}^{-1}$ for lower concentrations.

Results and Discussion

Geochemical Characterization of the Effluents in the SAT.

The chemical compositions of the different waters in the Yavne-2 SAT system are presented in Table 1. The values represent averages of the analyses carried out in the present research during 2004–2005. Large standard deviations in some of the components stem from the high temporal and spatial variability within the SAT system. The Cl^- concentration in the recharged effluents, $8.5 \pm 1.1 \text{ meq L}^{-1}$, was used to distinguish between the different wells and their waters (Figure 1). Wells having $\text{Cl}^- \geq 8.5 \pm 1.1 \text{ meq L}^{-1}$ were termed “100% wells” and are assumed to produce 100% reclaimed effluents. These wells include also the observation wells located adjacent to Yavne-2. “Mixed wells” are characterized by lower Cl^- concentrations, which depend on the degree of mixing with aquifer freshwater (Figure 2a), while the “unaffected wells” produce the background aquifer water. It should be noted that the latter vary spatially; higher Cl^- concentrations are generally found in the eastern parts of the Coastal Aquifer compared to its western parts. Over the years a gradual rise in the salinity of the entire aquifer took place (20); in the Shafdan area between 1987 and 2005, the Cl^- concentration in the western parts increased from 1.1 to 1.8 meq L^{-1} , whereas the concentration in the eastern side increased from about 3 to 4.4 meq L^{-1} .

Major Ions. During 2004–5, the concentrations of Na^+ , K^+ , Mg^{2+} , Cl^- , and SO_4^{2-} did not change significantly along the water flow path, from the Yavne-2 infiltration basin to the production wells (Table 1). This implies that, presently, the SAT system is in a dynamic steady state with respect to these components. This stands in contrast to the conditions that prevailed during the early stages of operation, when cation-exchange and adsorption reactions modified the major ion composition (21). The observed increase in Ca^{2+} and ALK concentrations of about 1 meq L^{-1} between the recharged effluents and the 100% wells suggests dissolution of CaCO_3 within the SAT system (21). Ion concentrations in the mixed

TABLE 1. Average Chemical Compositions of the Different Water Types Sampled during 2004–2005^a

	(meq L ⁻¹)				(mg L ⁻¹)				(μmol L ⁻¹)								
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	ALK	TDS	dissolved Mn	dissolved Fe	DIC	DOC	NKJT	NH ₄ ⁺	NO ₃ ⁻	DO	pH
recharged effluents	8.7 ± 1.2 <i>n</i> = 12	0.6 ± 0.1 <i>n</i> = 12	3.6 ± 0.3 <i>n</i> = 12	2.3 ± 0.2 <i>n</i> = 12	8.5 ± 1.1 <i>n</i> = 12	2.0 ± 0.2 <i>n</i> = 12	4.9 ± 0.4 <i>n</i> = 12	1020 ± 90 <i>n</i> = 12	0.6 ± 0.2 <i>n</i> = 12	1.4 ± 0.5 <i>n</i> = 12	5200 ± 600 <i>n</i> = 5	1100 ± 20 <i>n</i> = 1	380 ± 15 <i>n</i> = 1	340 ± 110 <i>n</i> = 4	40 ± 40 <i>n</i> = 10	90–470	7.5 ± 0.1 <i>n</i> = 2
vadose zone (0.5–9 m deep)	8.1 ± 1.2 <i>n</i> = 52	0.5 ± 0.1 <i>n</i> = 52	4.0 ± 1.2 <i>n</i> = 52	2.2 ± 0.2 <i>n</i> = 52	7.7 ± 1.6 <i>n</i> = 50	1.9 ± 0.2 <i>n</i> = 52	4.9 ± 0.6 <i>n</i> = 37	1000 ± 85 <i>n</i> = 34	0.2 ± 0.3 <i>n</i> = 57	0.4 ± 0.3 <i>n</i> = 57	5300 ± 1000 <i>n</i> = 14	na ^b	na ^b	0.7 ± 0.4 <i>n</i> = 8	320 ± 390 <i>n</i> = 48	na ^b	na ^b
perched horizon	9.0 ± 1 <i>n</i> = 2	0.5 ± 0.1 <i>n</i> = 2	4.1 ± 0.3 <i>n</i> = 2	2.2 ± 0.2 <i>n</i> = 2	9.2 ± 1.4 <i>n</i> = 2	2.1 ± 0.2 <i>n</i> = 2	4.6 ± 0.2 <i>n</i> = 2	1050 ± 80 <i>n</i> = 2	0.05 ± 0.05 <i>n</i> = 2	0.2 ± 0.2 <i>n</i> = 2	5000 ± 100 <i>n</i> = 1	300 ± 10 <i>n</i> = 1	60 ± 5 <i>n</i> = 1	0.2 ± 0.01 <i>n</i> = 1	130 ± 60 <i>n</i> = 2	100 ± 30 <i>n</i> = 2	7.0 ± 0.1 <i>n</i> = 1
water table, below Yavne-2	8.8 ± 0.1 <i>n</i> = 4	0.6 ± 0.1 <i>n</i> = 4	4.9 ± 0.2 <i>n</i> = 4	2.3 ± 0 <i>n</i> = 4	8.2 ± 0.6 <i>n</i> = 4	2.0 ± 0.2 <i>n</i> = 4	5.8 ± 0.7 <i>n</i> = 4	1090 ± 20 <i>n</i> = 4	0.6 ± 0.5 <i>n</i> = 4	0.2 ± 0.1 <i>n</i> = 4	8000 ± 600 <i>n</i> = 2	120 ± 0 <i>n</i> = 2	30 ± 0 <i>n</i> = 2	0.2 ± 0.1 <i>n</i> = 4	570 ± 100 <i>n</i> = 4	30 ± 30 <i>n</i> = 4	6.9 ± 0.1 <i>n</i> = 2
100% wells	9.1 ± 0.5 <i>n</i> = 43	0.6 ± 0.1 <i>n</i> = 43	5.0 ± 0.4 <i>n</i> = 43	2.3 ± 0.2 <i>n</i> = 43	9.0 ± 0.6 <i>n</i> = 43	2.0 ± 0.1 <i>n</i> = 43	5.7 ± 0.2 <i>n</i> = 43	1130 ± 40 <i>n</i> = 43	12 ± 14 <i>n</i> = 43	0.4 ± 0.4 <i>n</i> = 41	6500 ± 500 <i>n</i> = 41	120 ± 20 <i>n</i> = 26	30 ± 10 <i>n</i> = 42	0.2 ± 0.2 <i>n</i> = 36	420 ± 90 <i>n</i> = 43	50 ± 40 <i>n</i> = 39	7.1 ± 0.2 <i>n</i> = 43
mixed wells	6.2 ± 1.8 <i>n</i> = 17	0.4 ± 0.3 <i>n</i> = 17	4.7 ± 0.5 <i>n</i> = 17	2.5 ± 0.5 <i>n</i> = 17	6.7 ± 1.6 <i>n</i> = 17	1.4 ± 0.4 <i>n</i> = 17	5.3 ± 0.7 <i>n</i> = 17	920 ± 180 <i>n</i> = 17	0.04 ± 0.05 <i>n</i> = 17	0.4 ± 0.2 <i>n</i> = 17	6000 ± 1000 <i>n</i> = 17	50 ± 20 <i>n</i> = 8	20 ± 10 <i>n</i> = 17	0.06 ± 0.05 <i>n</i> = 15	450 ± 100 <i>n</i> = 17	100 ± 60 <i>n</i> = 17	7.2 ± 0.2 <i>n</i> = 17
eastern unaffected well, P/211	2.9 ± 0 <i>n</i> = 2	0.7 ± 0 <i>n</i> = 2	4.3 ± 0.1 <i>n</i> = 2	2.5 ± 0.1 <i>n</i> = 2	4.4 ± 0.1 <i>n</i> = 2	0.7 ± 0 <i>n</i> = 2	4.4 ± 0.1 <i>n</i> = 2	700 ± 35 <i>n</i> = 2	<0.04 <i>n</i> = 2	<0.4 <i>n</i> = 2	5100 ± 300 <i>n</i> = 2	<20 ± 10 <i>n</i> = 1	14 ± 10 <i>n</i> = 2	<0.1 <i>n</i> = 1	940 ± 15 <i>n</i> = 2	245 ± 10 <i>n</i> = 2	7.2 ± 0.2 <i>n</i> = 2
western unaffected well, P/2	1.4 ± 0 <i>n</i> = 2	0.1 ± 0 <i>n</i> = 2	3.4 ± 0.1 <i>n</i> = 2	1.1 ± 0 <i>n</i> = 2	1.8 ± 0 <i>n</i> = 2	0.3 ± 0 <i>n</i> = 2	3.6 ± 0 <i>n</i> = 2	425 ± 15 <i>n</i> = 2	<0.04 <i>n</i> = 2	<0.4 <i>n</i> = 2	3500 ± 0 <i>n</i> = 2	<20 ± 10 <i>n</i> = 1	16 ± 6 <i>n</i> = 2	0.03 ± 0.01 <i>n</i> = 1	280 ± 15 <i>n</i> = 2	215 ± 10 <i>n</i> = 2	7.4 ± 0.4 <i>n</i> = 2

^a The “100% wells” represents the observation and production wells that presently contain 100% reclaimed effluents; the “mixed wells” include the wells that pump mixture of reclaimed effluents and freshwater from the surrounding aquifer. The large deviations from the averages in some of the components stem from the high temporal and spatial variability of the SAT system (when *n* = 1 the analytical error is given), not analyzed

wells are generally lower than those of the 100% wells, as expected upon mixing with the aquifer freshwater.

Redox Sensitive Components: DOC, NKJT, Nitrate, and DO. The electron donors that drive the redox processes in the SAT system are DOC and the reduced nitrogen (N-Kjeldahl-NKJT) in the recharged effluents. Dissolved organic carbon (DOC) and NKJT concentrations drop from 800 to 1300 $\mu\text{mol L}^{-1}$ and 400–900 $\mu\text{mol L}^{-1}$ in the recharged effluents to 100–300 $\mu\text{mol L}^{-1}$ and $<60 \mu\text{mol L}^{-1}$ in the reclaimed effluents, respectively (Figure 2c, Table 1 and the data set of Mekorot Water Co.). Compared to oxidation processes, adsorption of DOC is probably a minor factor in reducing the DOC concentration. This is suggested by data from another infiltration basin of the Shafdan, where OM accumulation occurred only in the upper 1 m of the sediment and amounts to less than 6% of the total DOC recharged in that basin during its entire 23 years of operation (5). Low concentrations of DOC and NKJT in the perched horizon, only 7 m below surface, and in the water table region (Table 1) indicate that most (about 90%) of the recharged DOC is oxidized already in the vadose zone, during the early stages of infiltration.

The recharged effluents contain rather low levels of NO_3^- and high levels of NH_4^+ and organic-N (Table 1). During the oxygenic stage, nitrification within the vadose zone completely oxidizes the reduced N to NO_3^- (Table 1, Figure 2d). Yet, the somewhat lower total-N in the production wells as compared to the total-N in the recharged effluents (Figure SI-2) suggests that some of the ammonium is either adsorbed or that denitrification process also occur.

DO content in the infiltrating effluents may vary significantly due to seasonal and diurnal fluctuations in photosynthesis, respiration and water temperature. Indeed, the measured DO in the effluents in the infiltrating basin ranged between 90 and 470 $\mu\text{mol L}^{-1}$. Additional oxygen for the oxidation of the DOC and NH_4^+ in the infiltrating effluents is derived from atmospheric oxygen that is “pumped” into the vadose zone by the alternating flooding/drying regime of the infiltration basins. Overall, the oxidation processes reduced the final DO concentrations in the groundwater below the infiltration basin and in the 100% wells to $\leq 50 \mu\text{mol L}^{-1}$ (Table 1).

Manganese Reduction. The average Mn concentration in the 100% wells ($12 \mu\text{mol L}^{-1}$) is 20 times higher than the average Mn concentration in the recharged effluents ($0.6 \mu\text{mol L}^{-1}$), indicating that Mn is mobilized within the SAT system. It should be noted further that high Mn concentrations were found only in 100% wells (Figure 1), where the DO concentrations are $<50 \mu\text{mol L}^{-1}$ (Figure 4). Large heterogeneity in the Mn concentration characterize the aquifer (Figure 2b), where Mn concentrations as high as $40 \mu\text{mol L}^{-1}$ were also encountered in some of the wells. This heterogeneity may be caused by the heterogeneity of the aquifer rocks (e.g., variable clay content and horizons), different flow rates, local redox processes, Mn lability in various rock types, etc.

The first report on high Mn concentrations in the Shafdan wells dates to the end of 2000 (Figure 2b). Since then, Mn concentrations were continuously monitored in all wells. Prior to this, Mn was measured annually by Mekorot Water Co. only in four selected production wells around the Yavne-2 infiltration basin. A careful inspection of the Mn data from these wells reveals that increased Mn concentrations ($1\text{--}5.5\text{ }\mu\text{mol L}^{-1}$) appeared in two of the 100% wells (212, 217a; Figure 1) as early as the second half of the 1990s (see insert in Figure 2b). These observations suggest that Mn began its rise in the 100% wells already during the late nineties, while the sharp rise occurred during the 2000s.

It is suggested that the increase in Mn concentrations in the reclaimed effluents stems from reduction of Mn-oxides coupled to DOC oxidation under the suboxic conditions

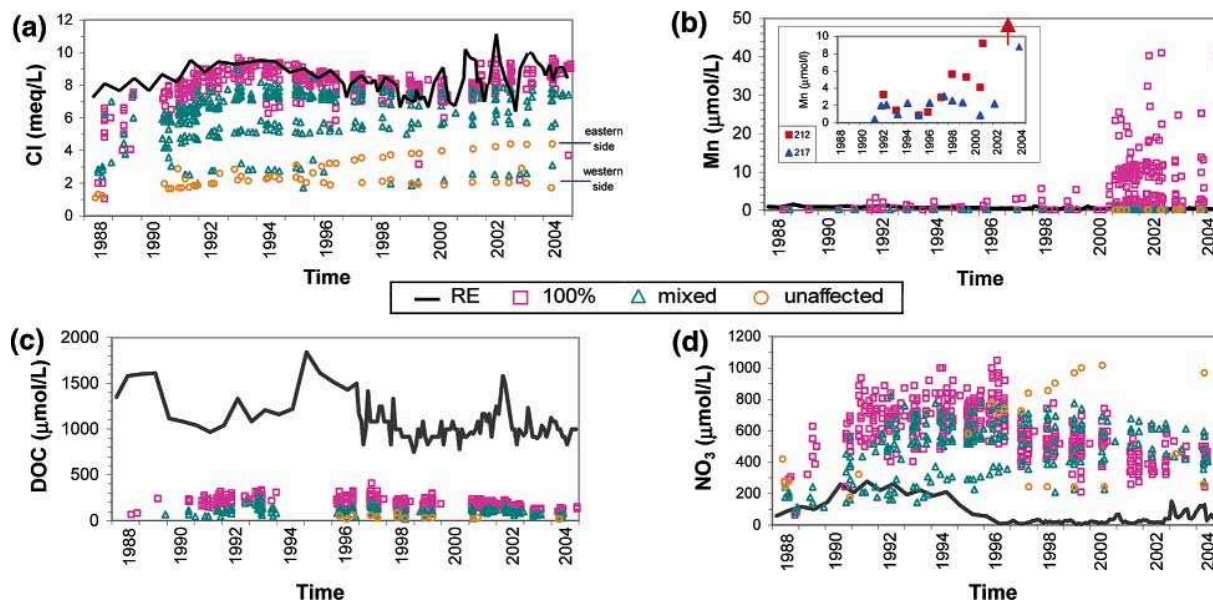


FIGURE 2. Concentrations of (a) Cl; (b) Mn (the inserted graph presents the relatively high Mn concentrations found in two wells during the 90's); (c) DOC; and (d) NO_3^- in the recharged effluents and the wells surrounding Yavne-2 during 1988–2004. RE, recharged effluents; 100%, wells that pump 100% effluents; mixed, wells that pump mixtures of effluents and freshwater; unaffected, wells that pump only freshwater. Note the difference in Cl concentrations in the groundwater east and west of the infiltration basin (data base of Mekorot Water Co.).

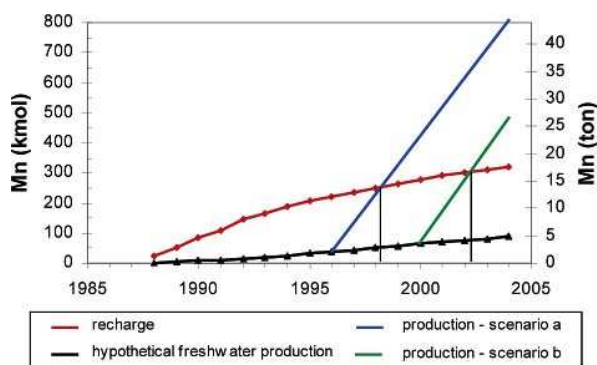


FIGURE 3. Cumulative Mn loads in the recharged effluents and in the reclaimed effluents. The two scenarios of bulk Mn withdrawal assume different times for the onset of Mn concentration increase (1996 and 2000). Also indicated is a hypothetical Mn load if the production wells were pumping only freshwater. The range where Mn production begins to exceed Mn recharge is marked by the vertical black lines.

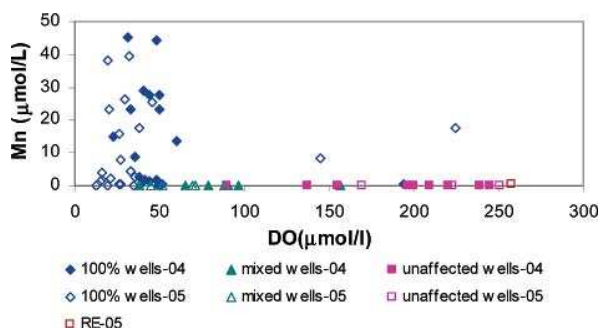


FIGURE 4. Mn concentrations versus dissolved oxygen (DO) in the wells around the Yavne-2 infiltration basin. The concentrations were measured in May 2004 and May 2005.

prevailing within the Yavne-2 SAT system. This Mn increase requires relatively little oxidation of the DOC that reaches the water table region below Yavne-2 ($120 \mu\text{mol/L}^{-1}$): To

attain Mn concentrations of $12 \mu\text{mol L}^{-1}$, the average Mn content in the groundwater, only $6 \mu\text{mol L}^{-1}$ DOC needs to be oxidized (eq 3). This is equivalent to only 5% of the DOC that reaches the water table region. The Mn is mobilized in groundwater containing high nitrate concentrations. According to the redox potential sequence (eqs 2 and 3), Mn reduction is not expected to occur at such high levels of NO_3^- , although presence of low levels of NO_3^- within the Mn reduction zone is common (8, 9). This paradox might be explained by Mn reduction occurring at specific sites within the aquifer, such as clay horizons, where the NO_3^- content has been reduced sufficiently to favor Mn reduction. Such localized reductions can also account for the overall decrease in the total-N in the reclaimed effluents (Figure SI-2). While locally decreased redox potential is possible, no indication for Fe-oxides and sulfate reduction were found; dissolved Fe remains low while SO_4^{2-} concentrations remains constant in the groundwater (Table 1).

Cumulative Mn Recharge and Recovery. In order to verify that Mn is mobilized from the aquifer rocks, a cumulative mass balance of input vs output of Mn over the period of operation of Yavne-2 was carried out.

The cumulative Mn input to the aquifer was calculated from the sum of products of the monthly volume of recharged effluents and their Mn concentrations. Accordingly, the amount of Mn recharged at Yavne-2 from March 1988 until November 2004, is about 320 kmol (17.5 ton; Figure 3).

The annual Mn withdrawal from the Yavne-2 field between 2001 and 2004, when Mn concentrations were already high, was calculated from the sum of Mn withdrawal by the 28 production wells during each year. According to this calculation, the average rate of Mn withdrawal is 96 kmol y^{-1} , with no significant differences between the years. Since the concentrations of Mn in the wells prior to 2001 are not known, the amount of Mn withdrawal prior to 2001 was estimated using two extreme scenarios, which are based on different timing of onset of Mn concentration rise (Figure 3): *a*, Mn increase began in 1996 (see insert of Figure 2b; this scenario is represented by the blue line in Figure 3); and scenario *b*, Mn rise began in 2000 (when most production wells show significant Mn increase; this scenario is represented by the

green line in Figure 3). The amount of Mn withdrawal in Yavne-2 is probably between these two estimates.

Both scenarios show that until the late 1990s, the recharged Mn in Yavne-2 (red line in Figure 3) exceeded the Mn withdrawal by the production wells, suggesting that Mn accumulated in the SAT system during the first years of operation. We rule out the possibility that substantial amounts of Mn leaked into the surrounding aquifer because (1) the total amount of reclaimed effluents pumped annually from the production wells is similar to amount of recharged effluents; (2) the Mn concentrations in the production wells were lower than the concentration in the recharged effluents during these years. Somewhere between 1998 and 2002 the cumulative Mn withdrawal at Yavne-2 field exceeded the total amount of recharged Mn. By 2004 the withdrawal Mn from Yavne-2 exceeded the recharged Mn by 27 and 8 tons according to scenarios *a* and *b*, respectively (Figure 3).

The Mn mass balance for the Yavne-2 SAT indicates clearly that the cumulative Mn pumped by the production wells since onset of operation is substantially larger than the Mn recharged with the effluents. The obvious conclusion is that the excess Mn was leached from the aquifer rocks. Simple calculation indicates that this Mn can easily be leached from the aquifer rocks whose Mn content in the Shafdan area is $\sim 40 \text{ mg kg}^{-1}$ (5). Assuming that (a) only 5% of this Mn is leached, (b) aquifer thickness of 50 m, and (c) leaching occurs only under the infiltrating basin, results in a total leached Mn of about 27 tons. In view of the fact that the distance between the infiltration basin and the production wells is about 500 m the sedimentary Mn reservoir in the Shafdan area is practically unlimited. Mn mobilization thus depends mainly on the mineralogy of the Mn solid phases, the content of labile OM, and the redox conditions in the aquifer.

Mn Mobilization in the Yavne-2 Field. The relatively low concentrations of Mn ($\leq 1 \mu\text{mol L}^{-1}$) within the vadose zone (0–9 m) and in the water table region below the infiltrating basins (Table 1, Figure SI-1) and the mass balance conducted above indicate that the Mn is mobilized mostly within the saturated zone. This mobilization probably occurs within the high Mn^{2+} inner zone of the 100% reclaimed effluents area defining a radius of $\sim 500 \text{ m}$ from the center of the infiltration basin of Yavne-2 (Figure 1). The circle separating the high Mn^{2+} inner zone and the low Mn^{2+} outer zone of the 100% reclaimed effluents forms a clear Mn front.

The bulk dissolved Mn^{2+} content in the groundwater within the inner zone is about 10 ton (calculated from the radius of 500 m, aquifer thickness of 50 m, porosity of 0.4 and average Mn concentration of $12 \mu\text{mol L}^{-1}$). This large Mn reservoir (about 100 times larger than the same groundwater volume containing background Mn concentration) is currently being replenished about once a year (the residence time of groundwater within the inner zone) by the intensive mobilization of Mn from the host rocks.

A simple Mn^{2+} mass-balance model that includes reduction–adsorption–advection terms can explain the formation and the dynamics of the Mn front assuming that (1) Mn reduction is limited by availability of labile OM that defines a minimum volume just below the infiltration basin; (2) The reduced Mn^{2+} is adsorbed on exchange sites within the aquifer; (3) The availability of reducible Mn-oxide in the aquifer rocks is much larger than the capacity of exchangeable Mn^{2+} ; (4) The Mn front advances in the direction of groundwater flow only when all the Mn^{2+} exchangeable sites are saturated; and (5) Rhodochrosite (MnCO_3) precipitation is not a significant process in the groundwater and therefore the mass-balance model does not require a precipitation term. This is based on thermodynamic calculations which show that the 100% wells (average Mn composition) are undersaturated with respect to rhodochrosite (SI-3). Furthermore, indirect evidence for this is found in the large

heterogeneity in the Mn concentrations; if rhodochrosite precipitates in the aquifer, then one would expect to see a constant Mn concentration which represents saturation at the wells' constant alkalinity and pH. Neglecting dispersion, the rate of change of manganese concentration ($[\text{Mn}^{2+}]$) has the following form (22):

$$\left(\frac{\partial[\text{Mn}^{2+}]}{\partial t}\right) = P_{\text{RD}} - v \cdot \left(\frac{\partial[\text{Mn}^{2+}]}{\partial x}\right) - S \quad (4)$$

Where P_{RD} is the reduction rate of Mn-Oxides; v is the velocity of the water; and S is the rate of adsorption of Mn^{2+} on the solid aquifer material ($S = \text{Mn}^{2+} K_D \cdot (\partial[\text{Mn}^{2+}]/\partial t)$ where $\text{Mn}^{2+} K_D$ is the Mn^{2+} distribution coefficient). As a first approximation, we assume that Mn reduction is constant and occurs only below the infiltration basin (see item 1 above), thus $P_{\text{RD}} = C_{|x \leq \text{infiltration}}$ and $P_{\text{RD}} = 0_{|x \geq \text{infiltration}}$.

Substituting for S in eq 4, the Mn^{2+} mass balance beyond the infiltration basin ($P_{\text{RD}}=0$) yields the Mn^{2+} retardation factor, R (the ratio between the flow velocity of the groundwater, v , and the advance velocity of the Mn^{2+} front, $v_{\text{Mn}^{2+}}$ (22)):

$$R = \frac{v}{v_{\text{Mn}^{2+}}} = 1 + \text{Mn}^{2+} K_D \quad (5)$$

According to eq 5, R can be estimated with two independent methods:

Velocity Ratio. It took some 8–12 years between initial Mn mobilization, assumed to have begun soon after onset of operation of the Yavne-2 plant, and the appearance of high Mn concentrations in the 100% wells. Over a distance of 500 meters between the infiltration basin and the 100% wells this translates to Mn velocity ($v_{\text{Mn}^{2+}}$) of $\sim 0.15 \text{ m d}^{-1}$. Since groundwater residence time in the SAT system is about 1 year, i.e., about 1.5 m d^{-1} , a retardation factor of ~ 10 is obtained.

Distribution Coefficient. $\text{Mn}^{2+} K_D$ in the Yavne-2 SAT system can be estimated from the composition of the reclaimed effluents, suite of exchange constants for major ions (22) and the cation exchange capacity (CEC) of the aquifer as determined from a published empirical formula (ref 23, Figure SI-4). The clay and OM contents in the sediments of the Coastal Aquifer in the Shafdan area is in the range of 0–25% and 0.1–0.5%, respectively (5). Assuming $\sim 10\%$ clays and $\sim 0.2\%$ OM (the two most important constituents determining the CEC of the aquifer), the value obtained for $\text{Mn}^{2+} K_D$ is 3, and thus yielding a retardation factor of ~ 4 .

Considering the rather large uncertainty in estimating $\text{Mn}^{2+} K_D$ that stems from the uncertainty in determining the CEC, the similarity in R using both estimates is quite remarkable. This similarity indicates that as suggested above, reduction and adsorptions are the main processes controlling Mn mobilization.

The dependence of $\text{Mn}^{2+} K_D$ on the CEC means that R strongly depends on the clay content within the aquifer and its spatial distribution. Hence, the rather large heterogeneity of clay in the geological section of Yavne-2 field may explain the large variability of the Mn^{2+} concentrations in the aquifer.

Finally we postulate that the well-oxidized mixed wells that are beyond the zone of high Mn content (Figures 1, 2b) will not turn Mn-rich. The process that buffers the rise of Mn^{2+} in the outer circle is oxidation and precipitation of Mn-oxides within the aquifer, similarly to the phenomenon blocking at present the irrigation pipes that are fed by Yavne-2 groundwater.

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Supporting Information Available

A cross section along the SAT system of Yavne-2 infiltration basin and the total-N concentrations in the recharged effluents and the 100% wells are presented in Figures SI-1 and SI-2, respectively. The calculation of rhodochrosite saturation index is presented in SI-3, and the CEC and K_D calculations are presented in SI-4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Chapter 6

Water-rock interaction during recharge of effluents to a sandy aquifer - field evidence and column experiments

6.1 Introduction

Groundwater recharge by effluents has a potential of drastically altering the composition of the aquifer water. Such active recharge is done as a tertiary treatment by soil aquifer treatment (SAT), as well as effluent injection through wells in coastal aquifers in order to prevent seawater intrusion ([Andelman, 1994](#)). Effluents and sewage also recharge groundwater as they leak from pipes, flow in streams or when used for irrigation. The change in the composition of the groundwater due to the recharge of the effluents may lead to intensive water-rock interactions ([Vengosh and Keren, 1996](#); [Greskowiak et al., 2005](#); [Kass et al., 2005](#); [Pavelic et al., 2007](#)). Water-rock interactions were mainly studied in coastal aquifers where seawater intrusion replaces the fresh groundwater ([Magaritz and Luzier, 1985](#); [Appelo and Willemssen, 1987](#); [Pulido-Leboeuf, 2004](#); [Sivan et al., 2005](#); [Lambrakis, 2006](#)).

One of the most important water rock interactions, which has also been studied in laboratory experiments, is cation exchange ([Valocchi et al., 1981](#); [Chapelle and Knobel,](#)

1983; Appelo et al., 1990; Appelo, 1994; Panagopoulos et al., 2004; Andersen et al., 2005). Many studies describe exchange between Ca^{2+} and Na^+ , whereby the Na^+ is adsorbed onto the sediments and the Ca^{2+} is released into the water, be it seawater or effluents (Magaritz and Luzier, 1985; Appelo and Willemssen, 1987; Panagopoulos et al., 2004). Another dominant process that takes place in carbonatic aquifers is dissolution of CaCO_3 (Appelo and Postma, 1996; Greskowiak et al., 2005; Pavelic et al., 2007). Carbonate dissolution enhances when the organic matter in the recharge water oxidizes to CO_2 . Both cation exchange and CaCO_3 dissolution has been identified in the Israeli coastal aquifer (Nadler et al., 1980; Sivan et al., 2005; Kass et al., 2005) and in particular in the unsaturated zone of the Shafdan plant (Idelovitch and Michail, 1984; Vengosh and Keren, 1996), which is discussed below.

The SAT of the Shafdan plant recharges pretreated effluents into the Israeli coastal aquifer as tertiary treatment. The quality of the recovered effluents from the aquifer is improved for unrestricted irrigation and incidental drinking. However, in the last several years particles of solid Mn-oxide appeared in the piping of the end users. At the same time high manganese concentrations appeared in the recovery wells, especially around one of the infiltration basins - Yavne 2, where this study was conducted.

This study aimed to describe the geochemical evolution of the effluents during their flow in the SAT system focusing on the conditions controlling the mobility and transport velocity of manganese. The present chapter deals mainly with the fate of the major ions during the flow of effluents in the Shafdan system aquifer. Field observations are explained in view of the results of laboratory simulations conducted using experimental columns filled with Shafdan sediments. The behavior of Mn in the experiments is shown for comparison but discussed in details in Chapter 7 below. It is concluded that cation exchange processes and the carbonate system modify the chemical composition of the recharged effluents.

6.2 Materials and Methods

The historical data on the chemical compositions of recharged effluents (RE) and the recovered groundwater from observation and production wells were provided by Mekorot

Water Co. Generally, the charge imbalance of the historical chemical data is less than 2% (water analyses with large charge imbalance were discarded).

The laboratory experiments of water-rock interactions were designed to simulate the geochemical evolution of effluents during their flow in an alluvial coastal aquifer. During each experiment, a solution similar in ionic composition to that of the effluents but with a variable Mn content was pumped through a column that was packed with natural sediments. A schematic presentation of the experimental setup is provided in Fig. 6.1 and the physical characteristics of the different experiments are presented in Table 6.1.

The sediment in all the experiments was red-brown sand sampled at the surface above the aquifer near the Shafdan plant. The sediment was dried at room temperature, crushed and sieved to grain size lower than 2 mm, and split to homogeneous samples. The solutions for the experiments (hereby referred to as 'artificial effluents') were prepared by dissolving appropriate weights of NaCl, KCl, CaCl₂, MgCl₂·6 H₂O, NaHCO₃, Na₂SO₄ and MnSO₄·4 H₂O in distilled water. The latter was first purged with a gas mixture of N₂ (95%) and CO₂ (5%) to remove dissolved oxygen and simulate the high partial pressure of CO₂ (PCO₂) content in the recharged effluents (see below). The compositions of the columns inflow and outflow solutions are presented in Table 6.2.

The sediments were packed into 20 cm long and 4 cm internal diameter columns. During the experiments, artificial effluents were continuously pumped into the columns with a

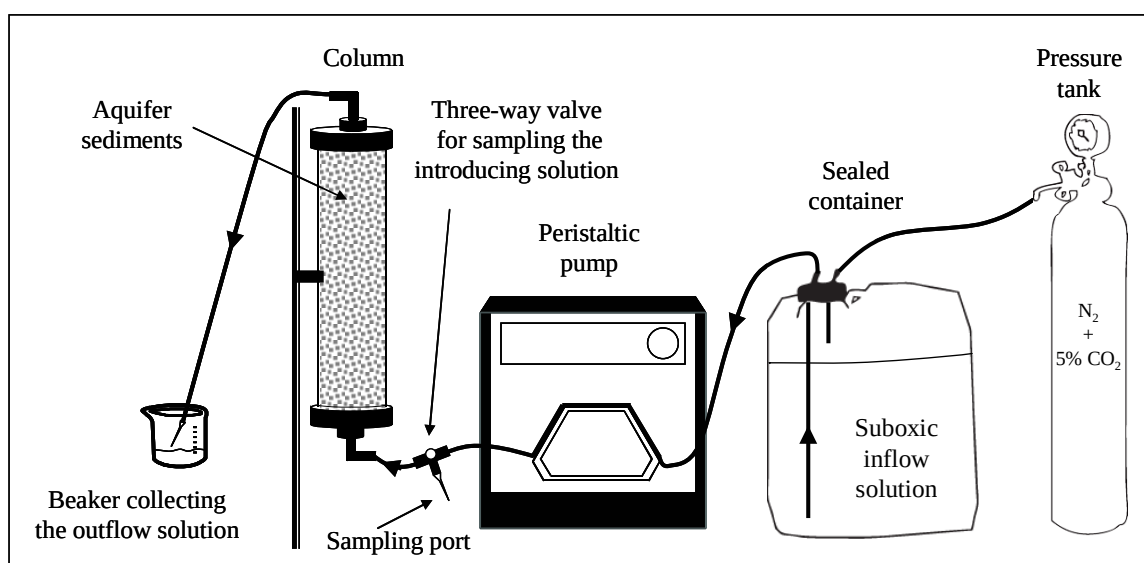


FIGURE 6.1: Schematic diagram of the column experiment.

peristaltic pump (Fig. 6.1). In order to simulate the suboxic conditions prevailing in the aquifer and to prevent oxidation of the soluble reduced Mn^{2+} , the artificial effluents container was continuously flushed with the gas mixture. The high PCO_2 in the mixture was intended to maintain the natural behavior of the carbonate system. The calculated PCO_2 in the aquifer according to the alkalinity and pH of the extracted water was found to be 25,760 ppm or about 2.6%. Water samples were collected throughout the experiments, before and after the columns. The water was sampled and stored in vials that were pre-flushed with He in order to maintain the redox conditions of the solution.

The cation exchange capacity (CEC) of the sediment and the cation distribution were determined in a separate experiment by eluting the sediments in the columns with a solution of 1M NH_4NO_3 at pH=7. The measurement included three steps: 1. flushing out of the originally adsorbed cations from the pristine (dried) sediment using the eluting solution. This provided the natural distribution of the CEC in the undisturbed sediment; 2. equilibrating the column with a 'concentrated artificial effluent', whose ion concentrations were double that of the 'artificial effluents', until the outflow solution stabilized at the composition of the inflow solution; and finally 3. flushing again the adsorbed cations by the eluting solution. The outflow solution was collected continuously to bottles containing concentrated HNO_3 so as to attain an acid/sample ratio of about 1:25 in order to prevent Mn^{2+} oxidation and CaCO_3 precipitation.

The content of adsorbed cations in the sediments were also determined by batch extraction with the eluting solution (1M NH_4NO_3 pH=7) at the end of the experiments. At the end of experiments the column's sediments were divided into five equal slices, which were immediately frozen and freeze-dried. For the cation extraction 1 g of the dry sediment was shaken in 40 mL of the eluting solution for 30 minutes. The mixture was then centrifuged and the supernatant was decanted and analyzed.

All samples (from the experiments and the extractions) were analyzed for their major cations content (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), Mn^{2+} and SO_4^{2-} . Analyses were carried out on a Perkin Elmer Optima 3300 ICP AES.

The clay mineral content was estimated by considering both the mineralogical composition and the chemical composition (e.g. Sandler et al., 2001). The sample was drenched in 0.2% Na_2CO_3 solution for ~ 1 day during which the fine particles were kept in suspension by ultrasonic bath and stirring. The $< 63 \mu\text{m}$ fraction was separated by sieving.

The $< 63 \mu\text{m}$ fraction was repeatedly centrifuged, decanted, and washed with distilled water and finally dried at 60°C . The mineralogical composition of this dried sediment was determined by XRD while its chemical composition was determined after fusion with LiBO_2 . Loss on ignition (LOI) was determined separately. The content of clay minerals was calculated from two parameters: the percentage LOI and MgO , after correction for the calcite and dolomite content and by comparison to known chemical composition of similar clays (Sandler, unpublished results).

For the determination of the CaCO_3 content in the sediments, $\sim 3 \text{ g}$ of crushed sample was put into a constant volume sealed canister ("bomb") equipped with a pressure gauge, into which 1:5 HNO_3 acid was added. A calibration curve was prepared by introducing different amounts of pure CaCO_3 into the bomb that produced different CO_2 pressures correlated to the CaCO_3 content.

TABLE 6.1: The characteristics of the column experiments. All columns contained the same red-brown sandy sediment which is characterized by clay content of $3.3 \pm 0.5\%$ and CaCO_3 content of $1.7 \pm 0.3\%$.

	UNITS	EXP 2	EXP 3	EXP 4	EXP 5	EXP 8	EXP 10
Solid weight	g	369	368	374	371	381	376
Pore volume	mL	102	102	89	111	90	92
Porosity	$\text{L} \cdot \text{L}^{-1}$	0.42	0.42	0.36	0.45	0.36	0.38
Bulk density	$\text{g} \cdot \text{mL}^{-1}$	1.51	1.50	1.53	1.51	1.56	1.54
Average discharge	$\text{mL} \cdot \text{h}^{-1}$	22.3	27.2	23	21.5	20	*
Average flow vel.	$\text{cm} \cdot \text{h}^{-1}$	4.2	5.2	5.1	3.8	4.4	*

* Flow rate was varied as part of the experiment

6.3 Column experiments

The chemical composition of the 'artificial effluents' inflowing and outflowing the columns as a function of the number of pore volumes transferred is given in Figs. 6.2 - 6.5 and in Appendices 8 - 11 . The number of pore volumes is the cumulative effluent volume that passed through the column normalized to the pore volume of the column sediment. This

normalization enables comparison between different experiments and between the experiments and the field observations. For the convenience of the following discussion, the first few milliliters of effluents that discharged from the column are defined to represent the chemical composition for pore volume equals unity.

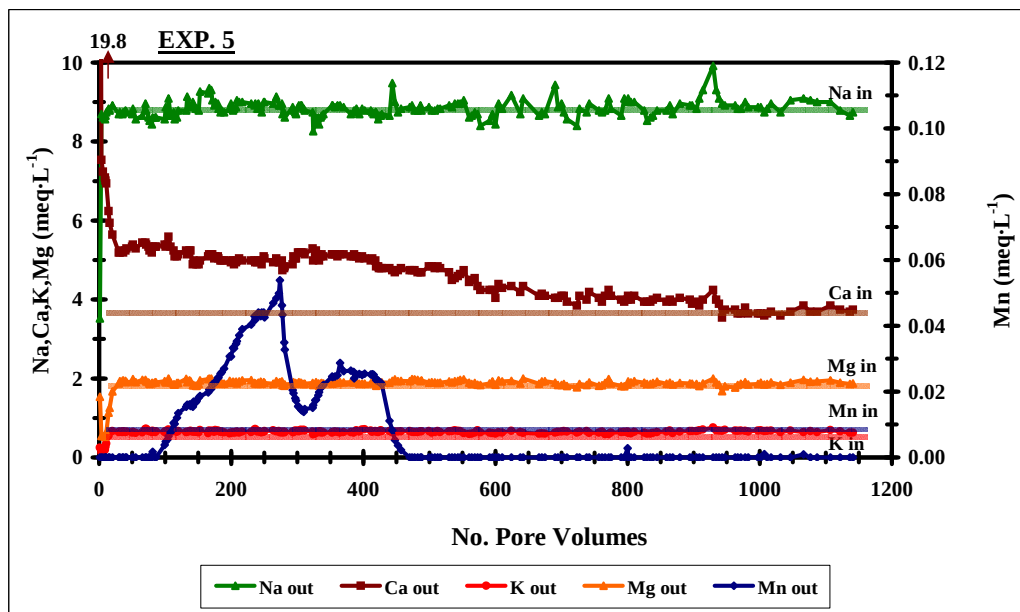


FIGURE 6.2: Breakthrough curves of the major cations and Mn in experiment 5. The concentrations in the inflow solution are marked by the solid horizontal lines.

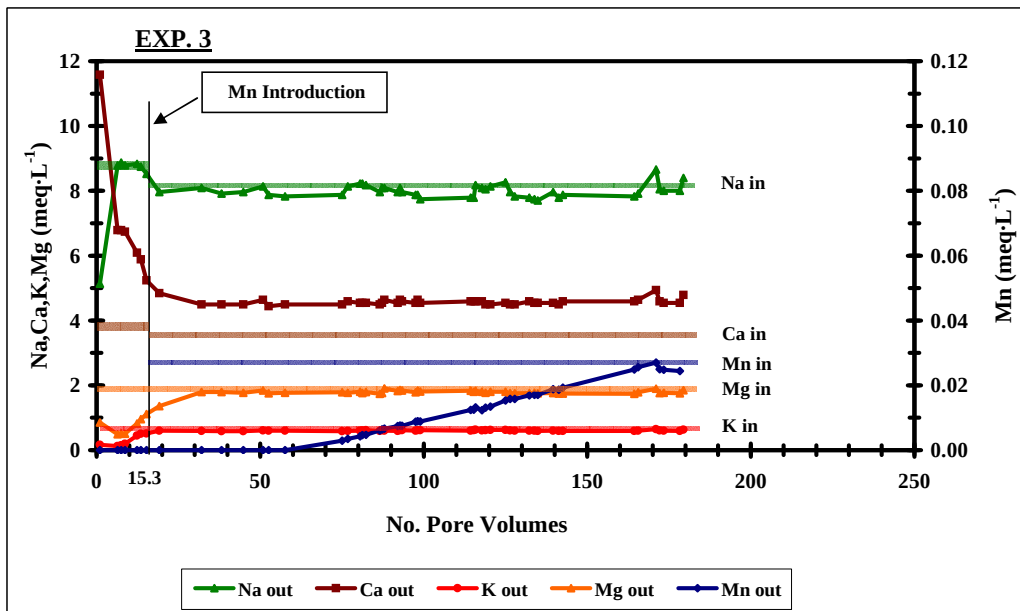


FIGURE 6.3: Breakthrough curves of the major cations and Mn in experiment 3. The concentrations in the inflow solution are marked by the solid horizontal lines.

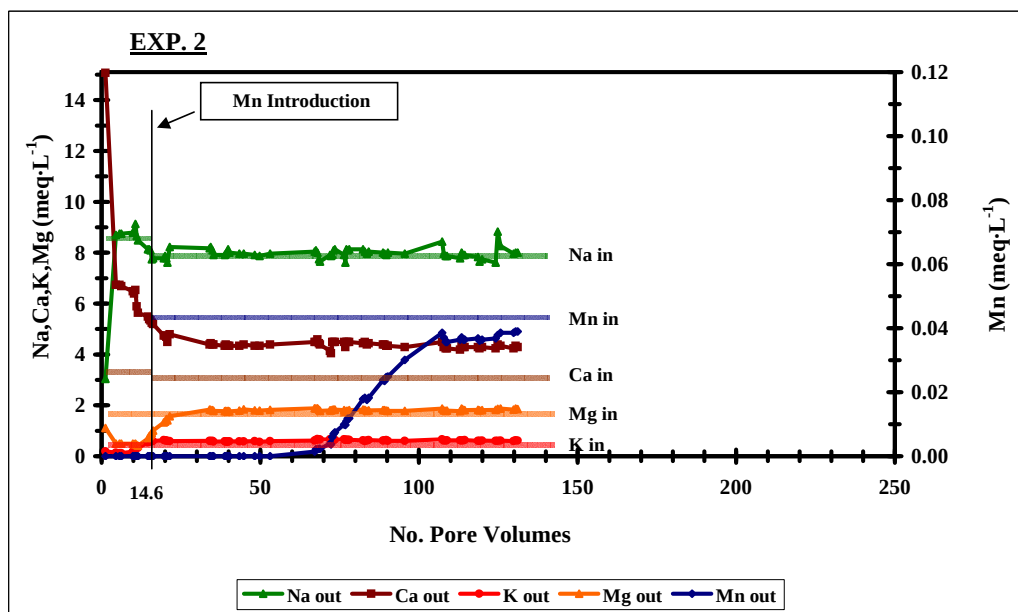


FIGURE 6.4: Breakthrough curves of the major cations and Mn in experiment 2. The concentrations in the inflow solution are marked by the solid horizontal lines.

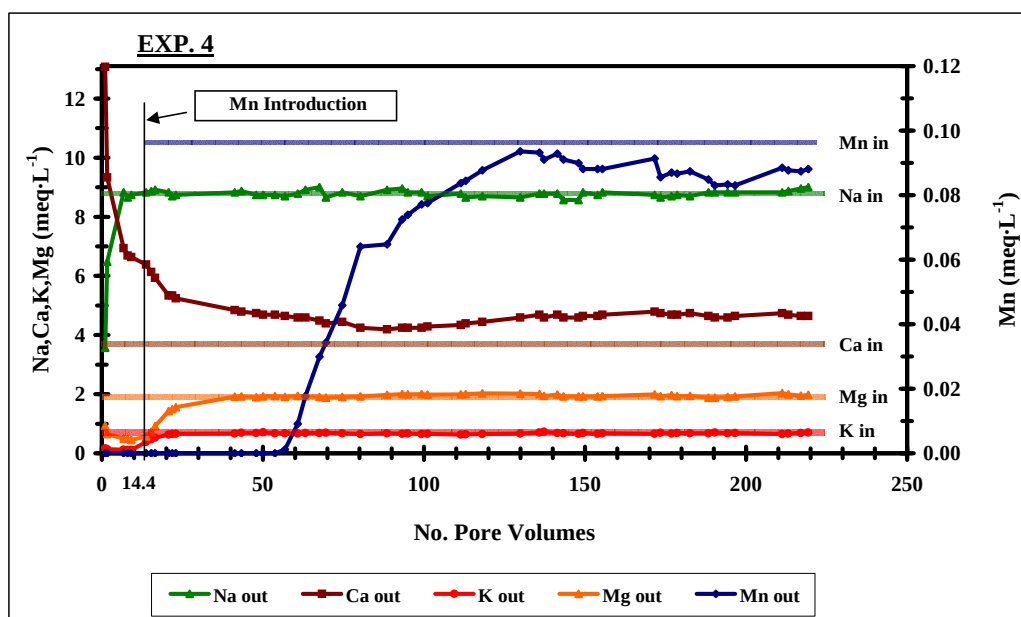


FIGURE 6.5: Breakthrough curves of the major cations and Mn in experiment 4. The concentrations in the inflow solution are marked by the solid horizontal lines.

The initial solution that emerged from the columns (at pore volume equals unity) in all experiments was significantly depleted in Na^+ , K^+ and Mg^{2+} and enriched in Ca^{2+} compared to the inflowing 'artificial effluents' (Figs. 6.2 - 6.5). Thereafter, the Na_{out}^+ , K_{out}^+ , and Mg_{out}^{2+} increased gradually towards the original concentrations in the inflow solutions while the Ca_{out}^{2+} decreased to a value that remained higher by about $1 \text{ meq} \cdot \text{L}^{-1}$ compared to the inflow concentration. The Mn_{out}^{2+} appeared in the outflow solution after more than 40 pore volumes, much after the major ions approached or attained equilibrium (Figs. 6.2 - 6.5). The behavior of Mn in EXP 5 (Fig. 6.2.) was different than in all other experiments, most likely due to technical problems that resulted in redox changes within the column, and is ignored hereafter. Detailed discussion of the Mn breakthrough is presented in Chapter 7. The average compositions of the inflow solutions and the outflow solutions after attaining equilibrium for the different experiments are presented in Table 6.2.

TABLE 6.2: Average chemical compositions of the inflow solutions and outflow solutions after attaining equilibrium in the column experiments.

Experiment Name	Analyzed Solution	Mn^{2+}	Na^+	K^+	Ca^{2+} ($\text{meq} \cdot \text{L}^{-1}$)	Mg^{2+}	Cl^-	SO_4^{2-}	Total Alkalinity*
Exp 5	inflow	0.011	8.8	0.7	3.7	1.9	9.3	1.9	3.9
	outflow		8.8	0.6	4.8	1.9	9.3	1.9	4.9
Exp 3	inflow	0.024	8.3	0.6	3.5	1.8	8.7	1.8	3.7
	outflow		8.0	0.6	4.6	1.8	8.6	1.8	4.6
Exp 2	inflow	0.046	8.2	0.6	3.4	1.8	8.7	1.8	3.5
	outflow		8.0	0.6	4.4	1.8	8.6	1.8	4.4
Exp 4	inflow	0.097	8.8	0.7	3.7	1.9	9.4	2.0	3.7
	outflow		8.8	0.7	4.6	2.0	9.2	2.1	4.8

* Estimated from charge balance calculations

6.3.1 Geochemical behavior

The geochemical behavior of the major ions in all four experiments was similar, showing five distinct consecutive stages in the chemical evolution of the water. Each stage is defined by a range of column pore volumes (see schematic plot in Fig. 6.6). The inflow

concentrations of all cations are similar to those in the outflow solutions in stage IV, except for Ca^{2+} , which is marked by a broken line. The concentration of Cl^- was not determined due to sample shortage, but is assumed to behave conservatively. The SO_4^{2-} concentration did not change throughout the experiments and remained equal to its inflow concentration, indicating a conservative behavior and negligible gypsum content in the column sediments.

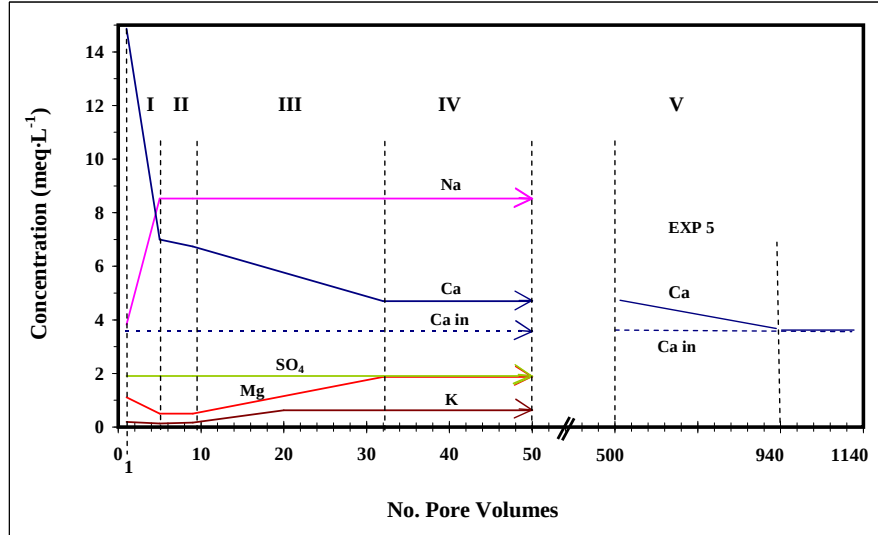


FIGURE 6.6: Semi schematic breakthrough curves of the major cations and SO_4^{2-} of the experiments. The concentrations in the inflow solution are the same as the concentrations in the output solution in stage IV, except for Ca^{2+} , which is marked by the broken line.

The different stages in the chemical evolution of the water are described below.

Stage I (1-5 pore volumes): increase in Na_{out}^+ from low concentrations to the attainment of the inflow concentration; a sharp decrease in Ca_{out}^{2+} from high concentrations to a value that remains higher than that in the inflow solution; K_{out}^+ and Mg_{out}^{2+} are lower than their inflow values and somewhat decrease in time (Figs. 6.2 - 6.6).

Stage II (5-9 pore volumes): K_{out}^+ and Mg_{out}^{2+} remain low and stable whereas the Ca_{out}^{2+} continues to decrease moderately.

Stage III (9-32 pore volumes): the stage begins with an increase in K_{out}^+ and Mg_{out}^{2+} and ends when they attain the inflow concentrations (at about 20 and 30 pore volumes, respectively); Ca_{out}^{2+} continues to decrease but at an enhanced rate as compared to its decrease in Stage II.

Stage IV (32 pore volumes onward): Na_{out}^+ , K_{out}^+ and Mg_{out}^{2+} maintain the inflow concentrations, while Ca_{out}^{2+} stabilizes at a value higher than that of the inflow solution by about $1 \text{ meq}\cdot\text{L}^{-1}$.

Stage V (at about 500 pore volumes onward): Ca_{out}^{2+} began to decrease and attained the inflow concentration value at about 940 pore volumes (Figs. 6.2, 6.6). This phenomenon marked the complete dissolution of CaCO_3 minerals within the column sediment, and was observed only during the longest experiment (EXP 5), which extended 8 months reaching 1140 pore volumes.

6.3.2 Geochemical processes and charge balances

In order to identify the processes that take place at each stage, charge balances were calculated. The outflow minus inflow charge balance was calculated for each cation in each stage of the four experiments (negative value means charge deficit in the outflow) by the following equation (see Fig. 6.7 for the calculation method):

$$EB_{i,j,k} = \left[(C_{i,j,k,b}^{out} - C_{i,k}^{in}) \cdot (n_j \cdot V_k) - \frac{1}{2} \cdot (C_{i,j,k,b}^{out} - C_{i,j,k,e}^{out}) \cdot (n_j \cdot V_k) \right] \quad (6.1)$$

where, $EB_{i,j,k}$ - charge balance (meq) for cation i at stage j during experiment k; C_{out} , C_{in} - outflow and inflow concentrations ($\text{meq}\cdot\text{L}^{-1}$), n - number of pore volumes, V - pore volume (L), b,e - beginning and end points of stage j, respectively. The average calculated $EB_{i,j,k}$ values for each cation at each stage are given in Table 6.3.

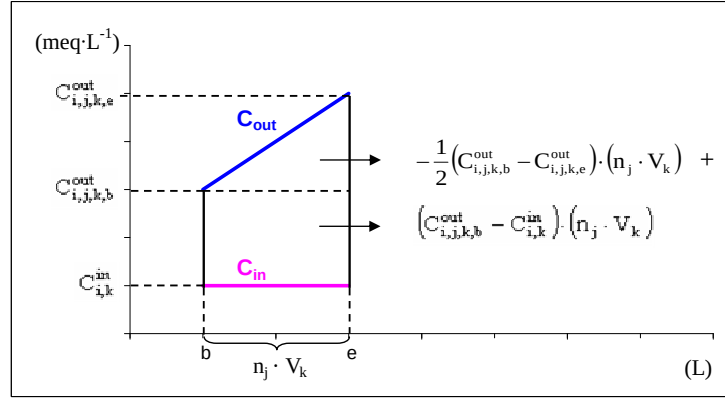


FIGURE 6.7: The calculation method of the individual cation excess or deficit at each stage in the four experiments in terms of equivalent (charge) units. Where, C_{out} , C_{in} – outflow and inflow concentrations ($\text{meq}\cdot\text{L}^{-1}$); i – cation; j – stage; k – experiment; n – number of pore volumes; V – pore volume (L); b, e – beginning and end points of stage j , respectively.

TABLE 6.3: All experiments averages of charge integrals and balances for the major cations at each stage. Positive numbers in rows #2 to #6 represent excess of the cation in the outflow solution while negative numbers represent deficit of the cation. In order to permit averaging of all experiments, the values of stage IV were integrated up to 50 pore volumes only, although this stage continues until the end of each experiment. The Ca^{2+} gain due to CaCO_3 dissolution was calculated assuming a constant dissolution rate as observed in stage IV.

Row #	Description	Stage I	Stage II	Stage III	Stage IV	Σ stages
1	number of pore volumes used for integration	4	4	23	18	49
(meq)					(meq)	(meq)
2	Na^+	-1.0	0	0	0	-1.0
3	K^+	-0.2	-0.2	-0.3	0	-0.7
4	Ca^{2+}	3.0	1.3	5.0	2.1	11.4
5	Mg^{2+}	-0.4	-0.5	-1.6	0	-2.5
6	Σ cations (Σ Rows #2 to #5) (= Excess Ca^{2+})	1.4	0.6	3.1	2.1	7.2
7	Ca^{2+} gain from CaCO_3 dissolution	0.5	0.5	2.7	2.1	5.8
8	Other Ca^{2+} gain (not from CaCO_3 dissolution) (Row #6 - Row #7)	0.9	0.1	0.4	0	1.4

The sum of the $EB_{i,j,k}$ values at each stage yielded positive values (Row #6 in Table 6.3), thereby indicating excess cation charge in the outflow solution over the inflow solution. In stage IV, this cation gain results clearly from Ca^{2+} excess since all other cations are fully balanced (Fig. 6.6, Table 6.3), indicating CaCO_3 dissolution. This dissolution

was probably enhanced by the high PCO_2 in the solution flowing into the columns. No change in the SO_4^{2-} concentration in the outflow solution (Fig. 6.6) shows clearly that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dissolution did not contribute to the observed Ca^{2+} gain. The constant difference between Ca_{in}^{2+} and Ca_{out}^{2+} (Figs. 6.2 - 6.6), throughout stage IV (even up to 500 pore volumes in EXP 5) indicates a constant carbonate dissolution rate. This dissolution is controlled both, by thermodynamics (i.e. CaCO_3 solubility) and kinetics (i.e. dissolution rate coefficient).

The calcite degree of saturation (Ω_{calcite}) for the inflow solutions during the experiments was calculated to be 0.09 (calculation parameters: $K_{sp} = 3.8 \cdot 10^{-9}$ (Stumm and Morgan, 1981); $[\text{Ca}^{2+}] = 1.8 \text{ mmol} \cdot \text{L}^{-1}$; $\text{alkalinity} = 3.7 \text{ meq} \cdot \text{L}^{-1}$; and $\text{pH} = 6.4$) and the Ω_{calcite} for the outflow solutions was 0.4 (calculation parameters: $K_{sp} = 3.8 \cdot 10^{-9}$; $[\text{Ca}^{2+}] = 2.3 \text{ mmol} \cdot \text{L}^{-1}$; $\text{alkalinity} = 4.7 \text{ meq} \cdot \text{L}^{-1}$; and $\text{pH} = 6.8$). Thus, the outflow solutions remained undersaturated with respect to calcite, suggesting that carbonate dissolution during the experiments was kinetically controlled. The increase by $1\text{-}2 \text{ meq} \cdot \text{L}^{-1}$ in the Ca^{2+} concentrations in the outflow solutions indicates that about $0.5\text{-}1 \text{ mmol} \cdot \text{L}^{-1}$ of CaCO_3 were dissolved during the 5 h residence time of the solution within the column while in contact with solid calcite. Since the rate of dissolution slows down as Ω_{calcite} approaches unity (see section 7.2.2), the final stage of dissolution, before attainment of saturation, may last for a long time.

To check this kinetic effect, an additional experiment (EXP 10) was carried out to examine how the flow velocity affects the Ca_{out}^{2+} (Appendix 12). After the experiment reached stage IV (i.e. constant Ca_{out}^{2+}), the flow velocity was lowered and then increased in several steps to minimum and maximum rates of one fifth and four times the original rate, respectively. Each flow velocity was maintained for at least 4 pore volumes. The outflow water composition at zero flow velocity was analyzed in one case, in which the flow was stopped for 4.5 d. The outflow solution collected afterwards, when flow was resumed, was taken to represent this composition.

In all experiments, the response of Ca_{out}^{2+} to change in flow velocity were small but clear (Fig. 6.8). Ca_{out}^{2+} responded in opposite direction to the change in flow velocity (Ca_{out}^{2+} decreased upon velocity increase and vice versa). The maximum change in Ca_{out}^{2+} was only ca. $\pm 7\%$ for flow velocity variations by more than 20 fold. Ca_{out}^{2+} increased by no more than 9%, even as a response to stopping the flow for a period of 4.5 d (see above

and Fig. 6.8). These observations further indicate that calcite dissolution proceeds at a fast rate when the degree of saturation is low (e.g. the inflowing composition), and is slowed down when the solution approaches equilibrium with respect to calcite.

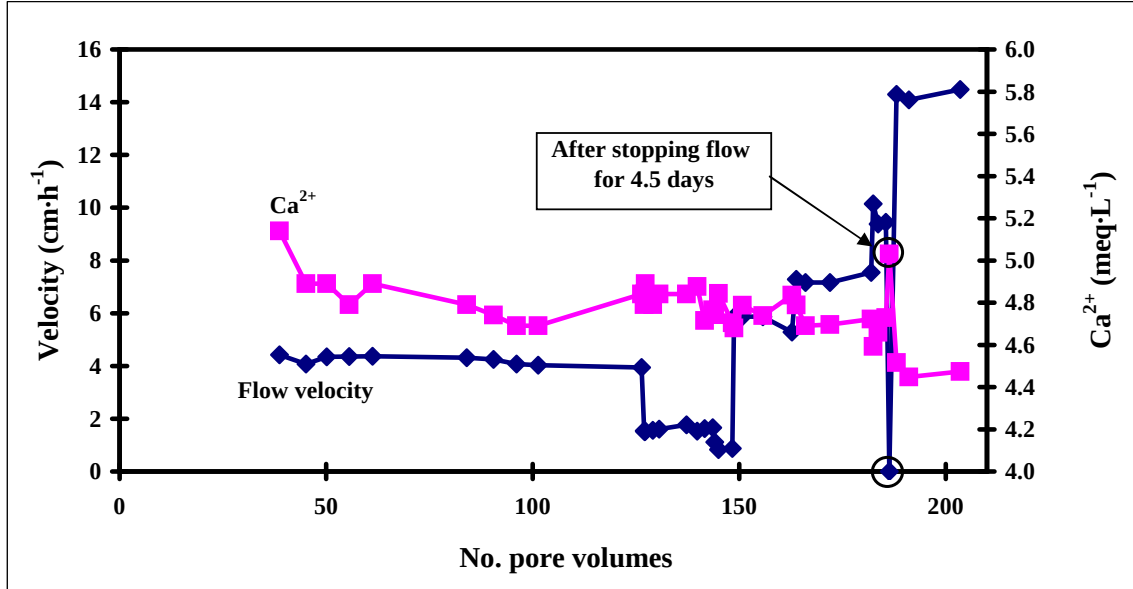


FIGURE 6.8: Response of Ca^{2+} concentrations in the outflow solution to change in the flow velocity in an experiment (EXP 10) designed to examine which mechanism controls the dissolution of CaCO_3 .

Ca_{out}^{2+} decreased in the final stage, stage V in EXP 5, and reached the value of Ca_{in}^{2+} (Figs. 6.5, 6.6). This indicates that the CaCO_3 in the column was completely dissolved. Indeed, at the end of EXP 5 no CaCO_3 was found in the sediment. All other experiments ended when $\text{Ca}_{out}^{2+} > \text{Ca}_{in}^{2+}$, at the end of these experiments, column sediments still contained 50-70% of their initial CaCO_3 content. Furthermore, the calculated weight of CaCO_3 that dissolved from the column was 5 g, (determined from the bulk excess Ca^{2+} in the outflow solution) very similar to the CaCO_3 content of the original column sediment (6.3 ± 1.1 g CaCO_3 , based on CaCO_3 content of $1.7 \pm 0.3\%$ and sediment weight of 371 g).

Active cation exchange is occurring during stages I-III as indicated by the deficits in Na^+ , K^+ and Mg^{2+} (as compared to their inflow concentrations) and the excess in Ca_{out}^{2+} that is higher than its value in stage IV. The observation suggests that when pristine aquifer sediments come into contact with Shafdan effluents, the Na^+ , K^+ and Mg^{2+} are adsorbed and Ca^{2+} is desorbed from the sediments. Na^+ achieves equilibrium very rapidly (at the end of stage I) while K^+ and Mg^{2+} continue to exchange with Ca^{2+} during 20 and

30 pore volumes, respectively (Fig. 6.6). Excess Ca^{2+} is maintained during stages I-III (row #6 in Table 6.3) indicating that CaCO_3 dissolution occurs during these stages in addition to the cation exchange.

The Ca^{2+} gain from CaCO_3 dissolution (as observed in stage IV) explains well the Ca^{2+} excess observed in stages II and III (see the similarity in row #7 and row #6 in Table 6.3, yielding a very small difference in row #8). In stage I however, a large Ca^{2+} excess of 0.9 meq (row #8 in Table 6.3) remained after accounting for CaCO_3 dissolution. This Ca^{2+} excess may result from proton buffering (exchange of Ca^{2+} by H^+ on column sediment). Ca^{2+} desorption in exchange of adsorbed H^+ was described during displacement of fresh water by seawater and vice versa (Appelo et al., 1990; Appelo, 1994). Displacement of Ca^{2+} by H^+ should imply a substantial pH increase in the initial outflow solution. Unfortunately, no pH data to corroborate this idea was collected on the outflow water during the column experiments.

The opposite process happens when seawater is replaced by freshwater in an aquifer: Ca^{2+} is adsorbed in exchange for Na^+ , K^+ and Mg^{2+} that are released into the pore water (Appelo, 1994). The order of elution during aquifer "freshening" is the same order that the cations reached equilibrium in the column experiments - first Na^+ , then K^+ and finally Mg^{2+} . Appelo, 1994 attributes this chromatographic pattern to increasing cation adsorption affinity. Accordingly, it is suggested that cation affinity is positively correlated with the duration of exchange prior to the attainment of equilibrium.

6.4 Cation Exchange Capacity (CEC) and cation distribution

Cation Exchange Capacity (CEC) is the capacity of sediment to adsorb positively charged ions, expressed usually in meq to 100 g dry sediment. The adsorption capacity depends on the specific surface of the sediment, increasing with clay and organic matter contents (Appelo and Postma, 1996). The cations that commonly occupy the CEC sites are Ca^{2+} , Mg^{2+} , Na^+ and K^+ . The equivalent fraction, β_I , of each exchangeable cation I^{i+} (having a charge i), is calculated as (Appelo and Postma, 1996):

$$\beta_I = \text{meq } I\text{-}X_i \text{ per } 100\text{g sediment} / \text{CEC} \quad (6.2)$$

where X indicate the soil exchanger.

Accordingly,

$$\beta_{Ca} + \beta_{Mg} + \beta_{Na} + \beta_K = 1 \quad (6.3)$$

The CEC and its cation distribution in the surface sediment of the Shafdan area were determined through three independent methods, as described hereafter.

6.4.1 Eluting experiments

Eluting experiments (EXP 8) were carried out on columns loaded with fresh surface sediments, similar to those used in the column experiments (Appendix 13). The CEC and the relative distribution of the cations were determined by eluting the adsorbed cations with a 1M NH_4NO_3 pH=7 eluting solution. The initial eluting desorbed the cations that had been adsorbed onto the pristine sediments when they were exposed as surface sediments and reacted with rain and surface water (Fig. 6.9A). Following this eluting, the column was equilibrated with 'concentrated artificial effluents' until the chemical composition of the outflow solution equaled that of the inflow solution. The column was then eluted again with the eluting solution, to obtain the cations relative distribution at the end of all column experiments (Fig. 6.9B). The second elution is also taken to represent the CEC and cations distribution of the aquifer when containing 100% effluents. To verify the result, the CEC was again measured at the end of EXP 5 (Fig. 6.9C, Appendix 14). The latter extended for more than 1100 pore volumes at the end of which the column was eluted with the eluting solution.

During the eluting experiments, the entire volume of the outflow solution was continuously collected into sampling vials. The CEC was calculated by summing the peak integrals as follows:

$$CEC = \left(\sum_{i=1}^4 \sum_{j=1}^n C_{i,j} \cdot V_j \right) \cdot \frac{100}{W} \quad (6.4)$$

where, i - cation, j - vial number, n - number of vials, C - concentration ($\text{meq} \cdot \text{L}^{-1}$), V - sample volume (L), W - column sediment dry weight (g).

The results show that all cations were completely eluted after one pore volume of the eluting solution was passed through the column (Fig. 6.9). For all major cations except

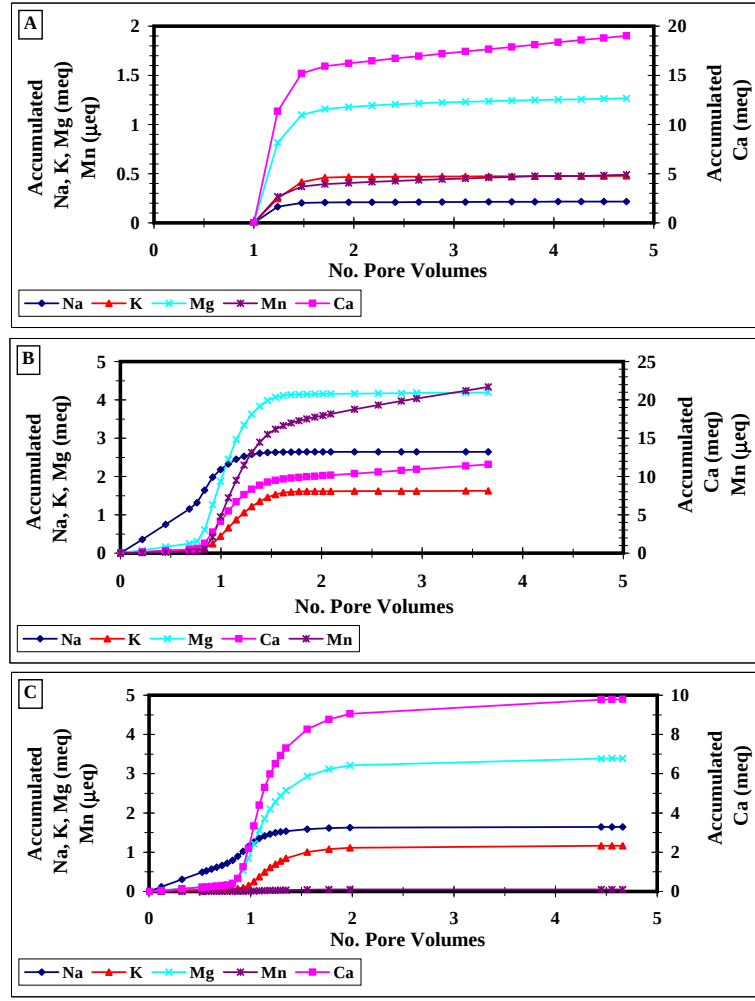


FIGURE 6.9: Accumulated cation amounts that eluted from the column in the outflow solution in three eluting experiments with a 1M NH_4NO_3 pH=7 eluting solution: A - adsorbed cations in the pristine surface sediment (step 1, CEC measurement); B - adsorbed cations after loading the column with the 'concentrated artificial effluents' (step 3, CEC measurement); and C - adsorbed cations at the end of EXP 5. The sum of the cation amounts gives the CEC of the sediment. Note that the major cations are given in meq units while the Mn is given in μeq

for Ca^{2+} the outflow concentration dropped to zero after one pore volume. Ca^{2+} continues to be flushed out from the column at low but constant concentration, suggesting that the eluting solution dissolves CaCO_3 from the column sediment. This small concentration was omitted from the Ca^{2+} peak integral calculation. The fractions of the cations (β_I) were calculated according to Eq. 6.2 for the pristine sediments and for the simulation experiments (Table 6.4).

Ca^{2+} is the most abundant adsorbed cation, comprising 90% of the CEC in the pristine surface sediment and about 60% after equilibration with the regular and concentrated

artificial effluents (Figs. 6.9, 6.10, Table 6.4). Mg^{2+} is the second most abundant cation, comprising about 20% of the CEC in the column experiments, while the monovalent cations, Na^+ and K^+ , are the least abundant, with $<10\%$ each (Fig. 6.10). The average CEC was calculated to be $4.4 \pm 0.4 \text{ meq} \cdot (100 \text{ g sediment})^{-1}$ (Table 6.4).

The adsorbed Mn^{2+} comprises a negligible fraction of the CEC (Table 6.4). The β_{Mn} for the column loaded with 'concentrated artificial effluents' was higher by factor of 50 than that of the pristine surface sediments ($100 \cdot 10^{-5}$ and $2 \cdot 10^{-5}$, respectively; Table 6.4). The trace quantities of adsorbed Mn enable calculating a reliable Mn distribution coefficient, facilitating the modeling of Mn mobilization (see Chapter 7).

TABLE 6.4: Cation Exchange Capacity (CEC) and the fractions of adsorbed cations (β_I) in pristine surface sediment and sediments loaded with artificial effluents as determined by column eluting experiments.

	CEC $\text{meq} \cdot (100 \text{ g sediment})^{-1}$	β_{Na}	β_{K}	β_{Ca}	β_{Mg}	β_{Mn}
Natural surface sediments (step 1, CEC measurement)	4.9	0.01	0.03	0.90	0.06	$2 \cdot 10^{-5}$
After equilibration with the concentrated artificial effluents (step 3, CEC measurement)	4.3	0.09	0.09	0.58	0.24	0.001
At the end of EXP 5	4.0	0.07	0.07	0.64	0.22	—

In order to verify that the eluting solution elutes all adsorbed cations, individual cation mass balances were carried out for the loading vs. eluting of the 'concentrated artificial effluent'. During the loading of the column, the entire outflow solution was collected and analyzed, thereby allowing determining the mass of each cation that was adsorbed onto the column. These masses were then compared to the calculated masses recovered from the elution of the loaded column showing recoveries of 92% for Na^+ , 97% for K^+ , 106% for Mg^{2+} , 224% for Ca^{2+} and 9% for Mn^{2+} . Considering procedural and analytical uncertainties, these results suggest complete recovery of Na^+ , K^+ and Mg^{2+} , extreme excess of Ca^{2+} and very low recovery of Mn^{2+} .

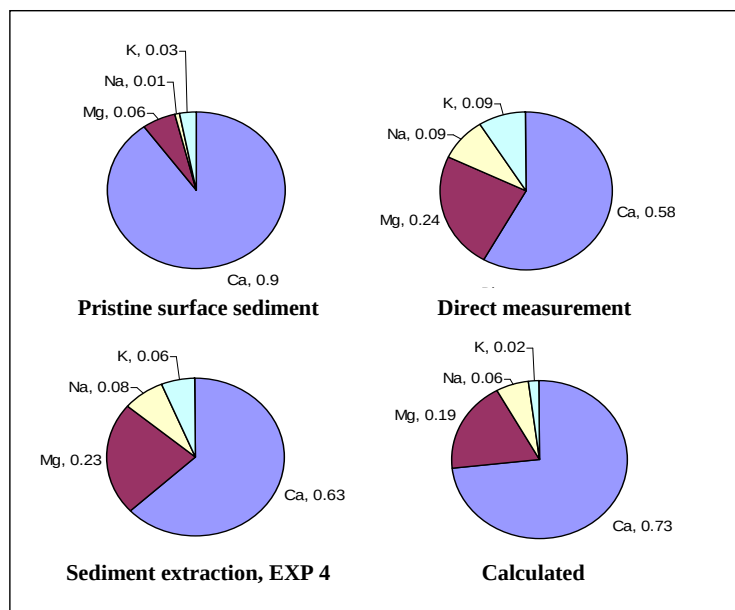


FIGURE 6.10: Cation fractions from the CEC in the pristine sediment according to direct measurement and at the end of the experiments according to direct measurement, sediment extraction and calculation.

The Ca^{2+} excess resulted most likely from dissolution of CaCO_3 . Nevertheless, it is unreasonable that during the eluting stage, when Ca^{2+} concentrations are extremely high (Appendix 13) due to the eluting process, CaCO_3 dissolution is responsible for the entire Ca excess. Rather, it is suggested that indeed it is all derived from desorption, but that the source of the excess Ca is CaCO_3 dissolution and immediate Ca^{2+} adsorption at an earlier stage, during the loading of the column with the 'concentrated artificial solution'. Indeed, the Ca^{2+} concentration in the outflow solution during the earlier stage of the loading was lower than the inflow concentration, indicating Ca adsorption. The low Ca concentration would also favor CaCO_3 dissolution (as observed in all column experiments). Given the fact that during that stage the exchange sites were loaded with NH_4^+ from the earlier elution, this new source of Ca^{2+} also exchanges with it, thereby adding to the Ca being adsorbed on the sediments.

The low Mn^{2+} recovery may indicate that a substantial amount of the adsorbed Mn is not exchangeable or that most of the Mn was not adsorbed during the loading stage but rather precipitated as MnCO_3 , and did not redissolve during the eluting stage. This stage was accompanied by massive CaCO_3 dissolution, which along with the high Mn content in the loading solution ($0.11 \text{ meq} \cdot \text{L}^{-1}$), would favor such MnCO_3 precipitation. The continuous supply of alkalinity from CaCO_3 dissolution most probably prevented

MnCO₃ dissolution during the eluting stage. A full discussion of MnCO₃ precipitation, kinetics and their role in Mn mobilization is provided in Chapter 7.

6.4.2 Adsorbed cation distribution at the end of the experiments

Batch extractions (with the eluting solution) of the pristine and the experimental sediments were conducted at the end of each column experiment (EXP 2-4), providing an additional estimate of the adsorbed cation fractions, β_I (Table 6.5). The experiment values are the averages and the standard deviations of five sub-samples that were taken along each column. Three sub-samples were eluted from the pristine surface sediments. The blank (eluting) solutions in EXP 2 and EXP 3 contained slight concentrations of the major ions, resulting in somewhat less reliable results. The high Ca²⁺ excess in the eluted sediments indicates that CaCO₃ was dissolved by the eluting solution (having a high solution/sediment ratio of 40:1), resulting in very large over-estimation of the adsorbed Ca and correct estimations for Na, K and Mg. The β_{Na} , β_K and β_{Mg} (Table 6.5) were calculated assuming that the CEC value was $4.4 \text{ meq} \cdot (100 \text{ g sediment})^{-1}$ (as determined in section 6.4.1 above) while β_{Ca} was calculated by difference ($\beta_{Ca} = 1 - (\beta_{Na} + \beta_K + \beta_{Mg})$). The estimated values of β_{Na} , β_K and β_{Mg} agree very well with the values calculated from the solution mass-balances, particularly for EXP 4 (section 6.4.1, Table 6.4, Fig. 6.10).

6.4.3 Empirical estimate of CEC and thermodynamic calculation of

β_{Ca} , β_{Na} , β_K and β_{Mg}

It is possible to calculate the CEC using the empirical formula developed by [Breeuwsma et al., 1986](#):

$$CEC \left(\text{meq} \cdot (100 \text{ g})^{-1} \right) = 0.7 \cdot (\%Clay) + 3.5 \cdot (\%Organic Carbon) \quad (6.5)$$

Substituting the measured clay mineral content in the experimental sediments of 3.3% and value of 0.1% of organic carbon, as a typical value in the studied area according to [Banin and Lin, 2003](#), yielded a CEC value of $2.7 \text{ meq} \cdot (100 \text{ g sediment})^{-1}$. This value is ca. 60% of the CEC estimated from the cations mass-balances conducted on the column experiments (Table 6.4, section 6.4.1).

TABLE 6.5: Exchangeable cations concentrations and fractions as determined in batch extractions of pristine surface sediment and at the end of the column experiments. It was assumed that the large Ca^{2+} excess resulted from CaCO_3 dissolution by the eluting solution and the "real" CEC is $4.4 \text{ meq} \cdot (100 \text{ g sediment})^{-1}$ (as estimated in section 6.4.1). The results represent average $\pm SD$ of three sub-samples of the pristine surface sediments and five sub-samples taken from the column at the end of each column experiment.

	Na^+	K^+	$^1\text{Ca}^{2+}$	Mg^{2+}	$^2\text{Ca}^{2+}$	$^2\beta_{\text{Ca}}$	β_{Na}	β_{K}	β_{Mg}
	$\text{meq} \cdot (100\text{g sediment})^{-1}$								
Pristine sediments	0.00 ± 0.00	0.12 ± 0.04	14.26 ± 1.14	0.18 ± 0.18	4.10 ± 0.21	0.93 ± 0.05	0.00 ± 0.00	0.03 ± 0.01	0.04 ± 0.04
EXP 2	0.01 ± 0.02	0.23 ± 0.06	10.80 ± 1.5	0.86 ± 0.10	3.30 ± 0.17	0.75 ± 0.04	0.00 ± 0.01	0.05 ± 0.01	0.20 ± 0.02
EXP 3	0.06 ± 0.04	0.23 ± 0.02	10.26 ± 2.97	0.69 ± 0.03	3.43 ± 0.07	0.78 ± 0.02	0.01 ± 0.01	0.05 ± 0.01	0.16 ± 0.01
EXP 4	0.33 ± 0.19	0.27 ± 0.01	10.57 ± 1.33	1.03 ± 0.04	2.77 ± 0.15	0.63 ± 0.03	0.08 ± 0.04	0.06 ± 0.00	0.23 ± 0.01

¹ Eluted Ca^{2+} .

² Estimated Ca^{2+} (see text).

The cation fractions, β_{Ca} , β_{Mg} , β_{K} and β_{Na} were calculated using the thermodynamic equilibrium constants (Appelo and Postma, 1996):

$$\beta_{\text{Ca}} = \frac{\beta_{\text{Na}}^2 \cdot [\text{Ca}^{2+}]}{K_{\text{Na}\backslash\text{Ca}}^2 \cdot [\text{Na}^+]^2} \quad (6.6)$$

$$\beta_{\text{Mg}} = \frac{\beta_{\text{Na}}^2 \cdot [\text{Mg}^{2+}]}{K_{\text{Na}\backslash\text{Mg}}^2 \cdot [\text{Na}^+]^2} \quad (6.7)$$

$$\beta_{\text{K}} = \frac{\beta_{\text{Na}} \cdot [\text{K}^+]}{K_{\text{Na}\backslash\text{K}} \cdot [\text{Na}^+]} \quad (6.8)$$

where, β_I - the equivalent fraction of cation I ; $[I^{i+}]$ - the molar concentration of cation I in the outflow solution; and $K_{\text{Na}\backslash I}$ - exchange coefficient between Na^+ and cation I . Substituting Eqs. 6.6 - 6.8 in Eq. 6.3 yields an expression for β_{Na} :

$$\beta_{\text{Na}}^2 \cdot \left(\frac{[\text{Ca}^{2+}]}{K_{\text{Na}\backslash\text{Ca}}^2 \cdot [\text{Na}^+]^2} + \frac{[\text{Mg}^{2+}]}{K_{\text{Na}\backslash\text{Mg}}^2 \cdot [\text{Na}^+]^2} \right) + \frac{\beta_{\text{Na}} \cdot [\text{K}^+]}{K_{\text{Na}\backslash\text{K}} \cdot [\text{Na}^+]} + \beta_{\text{Na}} - 1 = 0 \quad (6.9)$$

The parameters used for the calculations and the β_{Ca} β_{Mg} β_{Na} and β_K are presented in Table 6.6. The cation concentrations used in the calculations were those of the artificial solutions. The β_{Ca} β_{Mg} β_{Na} and β_K obtained in the calculations (Table 6.6) are similar to those estimated in sections 6.4.1 and 6.4.2 above (Tables 6.4, 6.5 and Fig. 6.10), indicating that the β_{Ca} β_{Mg} β_{Na} and β_K estimated for the Shafdan system are reliable.

TABLE 6.6: β_{Ca} β_{Mg} , β_{Na} , and β_K calculated using Eqs. 6.6 - 6.9 and the parameters used for calculations: cation concentrations in the outflow solutions of the column experiments and the cation exchange coefficients (from Appelo and Postma, 1996).

	$[I^{i+}]$ (mmol·L ⁻¹)	$K_{Na \setminus I}$	β_I
Ca²⁺	2.3	0.4	0.73
Mg²⁺	0.925	0.5	0.19
Na⁺	8.4	1	0.06
K⁺	0.6	0.2	0.02

6.5 Geochemical evolution of the effluents within the aquifer

The historical data shows that the chemical composition of the effluents in the aquifer changed in time and space during the first few years of operation, before a steady state composition was achieved (Figs. 6.11, 6.12, Appendix 5). This composition is similar to that of the RE, except for Ca²⁺ enrichment and periodic changes of other cations due to cation exchange. The temporal resolution of the data does not allow reconstructing the exact breakthrough curves of the major ions. In the followings, the effluents travel time as deduced from the Cl⁻ concentration is first discussed, followed by a discussion on the geochemical modifications of the groundwater.

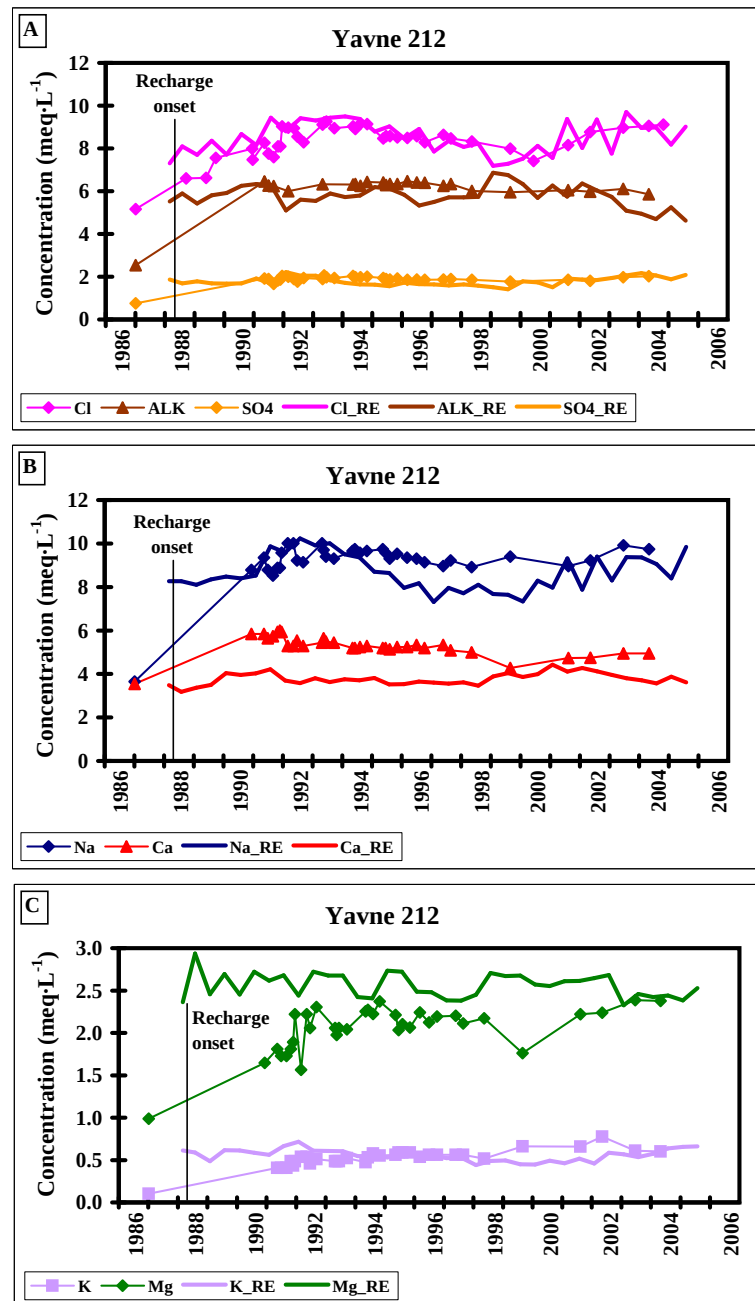


FIGURE 6.11: Concentrations of (A) Cl^- , alkalinity (ALK) and SO_4^{2-} ; (B) Na^+ and Ca^{2+} ; and (C) K^+ and Mg^{2+} in the recharged effluent (RE, smooth lines) and in production well - Yavne 212 (lines with points), located 540 m from the infiltration basin, during 1988-2005.

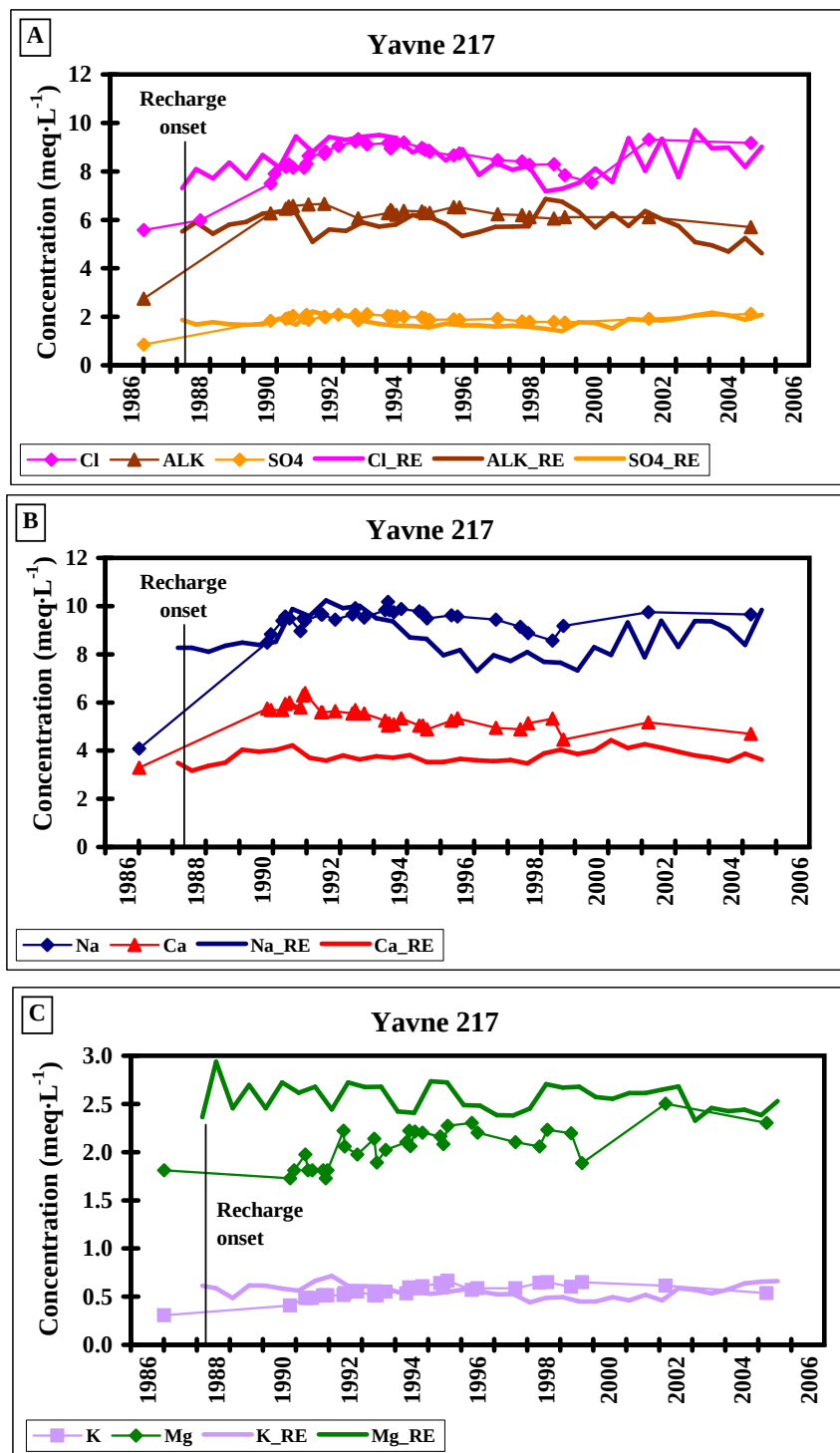


FIGURE 6.12: Concentrations of (A) Cl^- , alkalinity (ALK) and SO_4^{2-} ; (B) Na^+ and Ca^{2+} ; and (C) K^+ and Mg^{2+} in the recharged effluent (RE, smooth lines) and in production well - Yavne 217 (lines with points), located 350 m from the infiltration basin, during 1988-2005.

6.5.1 Effluents travel time

In order to distinguish between concentrations that are modified due to mixing of different waters in the aquifer and those due to geochemical processes, only wells that recover 100% effluents were investigated. The conservative element Cl^- was used to determine effluents travel time within the aquifer. This was conducted by plotting for each of the 100% production wells (Fig. 3.1) the time passed from the start of recharging effluents in Yavne-2 basin to the date in which Cl^- concentration reached its value in RE (Fig. 6.13; red marks). The Cl^- 'travel time' data were fitted by a cylindrical piston flow model (solid red line in Fig. 6.13) assuming a radial flow within a cylindrical aquifer saturated with RE, where the infiltration basin is located at its center (Fig. 6.14). The equation used to calculate the model 'travel time', t_r , was:

$$t_r = \frac{\pi \cdot Z \cdot \varepsilon \cdot (r^2 - r_{basin}^2)}{Q} \quad (6.10)$$

where, r - radial distance from the center of the infiltration basin (m), Z - aquifer thickness (m), ε - porosity, r_{basin} - radius of the infiltration basin (m), Q - annual effluents recharge ($\text{m}^3 \cdot \text{y}^{-1}$).

Eq. 6.10 ignores the water level gradient resulting from the hydrological mound formed by effluents recharge, the dispersion within the aquifer and preferential flow paths due to aquifer inhomogeneity. This approach, however, provides a first order estimate for the expected travel time. The parameters used for calculation were: $20 \cdot 10^6 \text{ m}^3 \cdot \text{y}^{-1}$ for the average yearly effluents load; 150 m for the infiltration basin radius; 60 m aquifer thickness; and 0.4 aquifer porosity. Best fit was attained when a lag time (constant time interval) of 19 months was added to the calculated curve (Fig. 6.13). It is likely that this lag time represents the overall time required to: 1. wet the unsaturated zone; 2. replace the groundwater column in the cylinder beneath the infiltration basin; and 3. build the groundwater mound which drives the flow. The longer 'travel time' of a retarded species is demonstrated by the K^+ plot (Fig. 6.13) The best fit for the K^+ 'travel time' suggests that its retardation factor is 2 (see discussion at the end of section 6.5.2. below).

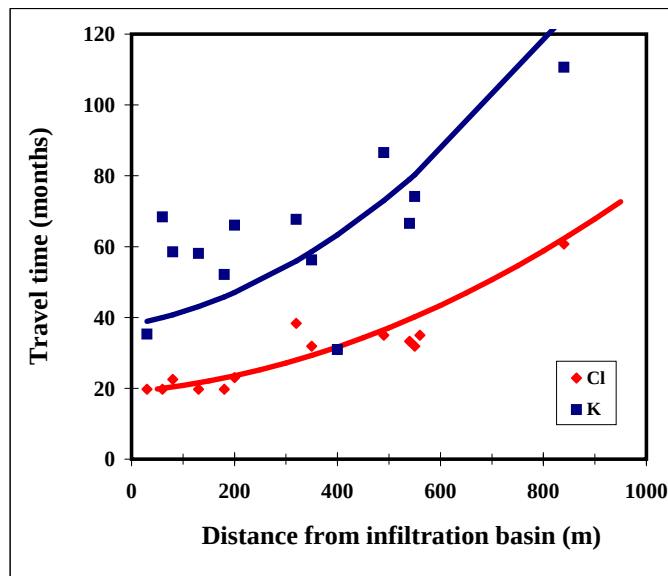


FIGURE 6.13: 'Travel time' (defined as the time required to attain 100% RE concentrations) of Cl^- (solid red diamonds) and K^+ (solid blue Squares) versus distance from the infiltration basin. The solid lines are the model times calculated as cylindrical radial flow (Eq. 6.10). Cl^- curve was calculated assuming yearly discharge of $20 \cdot 10^6 \text{ m}^3$, aquifer thickness of 60 m and porosity of 0.4 and K^+ curve was calculated assuming its retardation factor is 2 (twice the Cl^- 'travel time'). The markers represent the first appearance of the cations in their RE concentrations in wells at different distances from the basin.

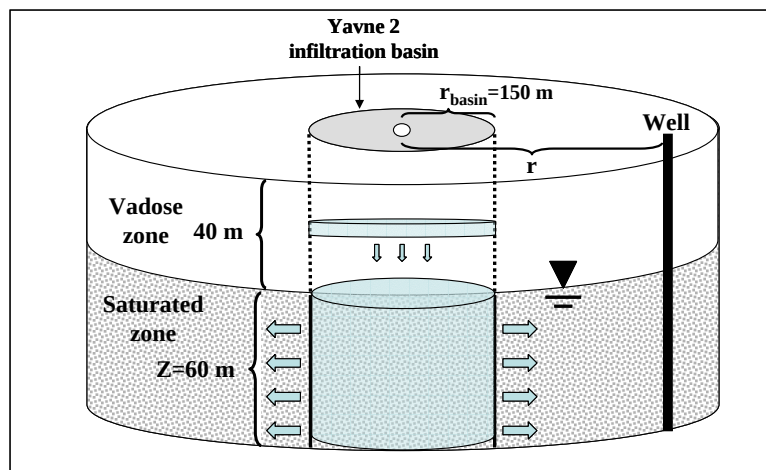


FIGURE 6.14: A schematic diagram depicting radial piston flow from a cylinder located in the aquifer below the infiltration basin, used for the theoretical calculation of travel time (Eq. 6.10).

6.5.2 Geochemical evolution

The reconstruction of the geochemical evolution of the effluents within the aquifer is based on comparison between the RE composition and the composition of the recovered effluents pumped from wells producing 100% effluents. The following discussion describes the behavior of the major ions.

SO₄²⁻: The groundwater attains the RE SO₄²⁻ concentrations contemporaneously with Cl⁻ (Figs. 6.11A, 6.12A). This suggests that SO₄²⁻ is also a conservative component in the SAT system and is not involved in any process in the subsurface.

Ca²⁺ and alkalinity: The Ca²⁺ concentrations in all production wells are higher than those in the RE by 1-2 meq·L⁻¹ (Figs. 6.11B, 6.12B), with no apparent temporal variations. Similarly to the behavior of Ca²⁺ in the column experiments, the Ca²⁺ excess resulted from an ongoing CaCO₃ dissolution that started at the onset of operation. The ~ 1.0 value calculated for the saturation degree with respect to calcite, $\Omega_{calcite}$ ($[Ca^{2+}] = 2.65 \text{ mmol}\cdot\text{L}^{-1}$; alkalinity = 6.2 meq·L⁻¹; and pH=7.2) indicates that Ca²⁺ reached its saturation concentration for the aquifer conditions. Cation exchange may also affect Ca²⁺ behavior as demonstrated in the column experiments (see above).

No rise in alkalinity equivalent to the Ca²⁺ increase was observed as a result of carbonate dissolution (Figs. 6.11, 6.12). It is possible therefore that the alkalinity buffered strong acid that was produced in the aquifer during nitrification of NH₄⁺ (the main nitrogen species in the RE) according to the reaction:



According to the composition of the RE, nitrification may release $\sim 1 \text{ mmol}\cdot\text{L}^{-1}$ of H⁺ when the NH₄⁺ or organic-N content of the RE ($\sim 0.5 \text{ mmol}\cdot\text{L}^{-1}$, see Figs. 3.4B, 3.5) was oxidized to NO₃⁻ within the aquifer. This H⁺ may have neutralized the increase in alkalinity that should have resulted from CaCO₃ dissolution.

Na⁺: The groundwater reached RE Na⁺ concentrations within the first years of operation. Thereafter, during 1995-2000, Na⁺ concentrations in most wells rose above the RE concentrations (Figs. 6.11B, 6.12B, Appendix 5). This rise reflects most probably desorption of Na⁺ from the aquifer sediments as a response to the decrease in the Na⁺ concentration in the RE (Figs. 6.11B, 6.12B, appendix 5). It is most likely that prior to 1995, when RE contained higher Na⁺ concentration, the Na adsorbed on the aquifer

sediments was also higher. It should be noted however that low Na^+ concentrations (relative to RE) were not observed soon after the onset of operation of the Yavne-2 plant, when the aquifer was still actively adsorbing Na. This is most likely due to the scarcity in the data from that period. Low Na^+ concentrations (relative to RE) were observed for few months up to 2 years in wells of the Soreq infiltration basin, indicating that Na^+ was adsorbed during the initial stage of the SAT operation (Idelovitch and Michail, 1984).

The scenario described above is examined quantitatively below by calculating (using Eqs. 6.6-6.9) the change in adsorbed cation fractions (β_I) before (1994) and after (1997) the change in RE composition (Table 6.7). This allows assessing if the decrease in RE Na^+ concentration (after 1994) may cause Na^+ desorption in a magnitude equivalent to the observed Na^+ concentration increase. The 1994-1997 change in β_I can be translated to the corresponding maximum change in groundwater cation concentration (equivalents of cation adsorbed/desorbed per one pore volume). The calculations were conducted as a single step without iterations to find the optimal β_I (the changes in cation concentrations were not used to backward calculate a new β_I and so on until converging to a constant β_I). The CEC used in the calculations was $4.4 \text{ meq} \cdot (100g \text{ sediment})^{-1}$, similar to that of the sediment used in the column experiments (but much higher than the aquifer's CEC, as will be discussed in the following section). This calculation method, therefore, resulted in a significant overestimation of the cation amounts adsorbed/desorbed following the change in the composition of the RE.

The calculation indicates that the decrease in the RE Na^+ concentration results in Na^+ desorption from the aquifer's sediments and Mg^{2+} (as well as some Ca^{2+}) adsorption. Indeed, decrease in Mg^{2+} concentration was also observed. The calculated magnitude of Na^+ increase is however too small because the observations showed a Na^+ excess (over RE) of about $1 \text{ meq} \cdot L^{-1}$ that lasted for 5 y (1995-2000, see Figs. 6.11, 6.12). Assuming groundwater residence time of one year (Chapter 5), the $1.32 \text{ meq} \cdot L^{-1}$ of calculated Na^+ increase (Table 6.7) may account for only $\sim 20\%$ of the observed Na^+ increase. This discrepancy is further emphasized given that the CEC estimated for the aquifer is about one order of magnitude lower than that of the column sediments (see discussion below). Thus, the excess and prolonged desorption of Na^+ from the sediments in response to change in the RE composition remains unsolved.

TABLE 6.7: Cation fractions and the calculated (maximum) corresponding change in their groundwater concentrations following change in the RE composition between 1994 and 1997. $[I^{i+}]$ - cation concentration in the RE, including CaCO_3 dissolution; ΔI - change in groundwater concentration. The parameters used for calculations were: CEC of $4.4 \text{ meq} \cdot (100 \text{ g sediment})^{-1}$, bulk density of $1.5 \text{ g} \cdot \text{mL}^{-1}$ and porosity of 0.4. Positive ΔI values represent cation concentration increase (as compare to RE) in groundwater while negative values represent decrease.

Cation	¹ $K_{\text{Na}\backslash I}$	1994		1997		
		$[I^{i+}]$ (mmol · L ⁻¹)	β_I	$[I^{i+}]$ (mmol · L ⁻¹)	β_I	ΔI (meq · L ⁻¹)
Ca ²⁺	0.4	2.65	0.713	2.55	0.715	-0.33
Mg ²⁺	0.5	1.21	0.208	1.19	0.214	-0.99
Na ⁺	1	9.36	0.061	7.96	0.053	1.32
K ⁺	0.2	0.55	0.018	0.53	0.018	0

¹ from [Stumm and Morgan, 1981](#)

Mg²⁺ and K⁺: The rise in Mg²⁺ and K⁺ concentrations in the production wells lag behind the rise in the Cl⁻ concentration and their breakthrough curves are identified in most wells (Figs. [6.11](#), [6.12](#), Appendix 5). In a few wells the breakthrough curves include also an initial stage of low and constant concentrations before the increase towards the RE concentrations. This behavior is common when cation exchange is the dominant process ([Beekman and Appelo, 1990](#)).

K⁺ travel time should be longer than that of Cl⁻ by a constant, which is the retardation factor, ^KR. Indeed, multiplying the Cl⁻ travel times, as calculated by Eq. [6.10](#), by a retardation factor of 2 yields a curve that correlates well with the observed K⁺ travel time (Fig. [6.13](#)), thereby providing a good estimate for the retardation factor of K⁺ in the aquifer.

The Mg²⁺ stabilized at a value lower by $0.2 - 0.8 \text{ meq} \cdot \text{L}^{-1}$ than its RE concentration (Figs. [6.11](#), [6.12](#)). The attainment of this stable, but low, concentration coincided in time with the decrease in RE Na⁺ concentration. Thus, it appears that the change in RE Na⁺ concentration, which induced Na⁺ desorption from the sediments, is accompanied by enhanced Mg²⁺ adsorption as demonstrated by its negative ΔI (Table [6.7](#)). The magnitude of the observed Mg²⁺ decrease during 1995-2000 did not fully balance the Na⁺ increase in the groundwater (Mg²⁺ decreased by only 0.2-0.8 meq·L⁻¹ while Na⁺

increased by $\sim 1.0 \text{ meq}\cdot\text{L}^{-1}$ over the same 5 year period). It is suggested therefore that the additional desorbed Na^+ was exchanged with Ca^{2+} adsorbed. The adsorbed Ca^{2+} was replaced with "new" Ca^{2+} originated from carbonate dissolution.

6.6 Comparison between the experiments and field observations

Cation exchange and CaCO_3 dissolution were identified as the main processes that change the chemical composition of the effluents during their flow in the aquifer, as observed in both the field and the column experiments. However, their behavior in the two systems was different due to:

1. The homogenous red-brown sand used in the experiments represents an intermediate composition containing enough clay minerals to allow significant adsorption and cation exchange while maintaining flow velocities similar to those in the aquifer. Such a sediment type however appears only as sporadic clayey and sandy horizons while the aquifer is comprised mainly of calcareous sandstones. It is concluded therefore that the red-brown sand used in the experiments has higher CEC than the "real" aquifer, and hence the exchangeable cations in the aquifer should have shorter retardation times than in the experiments.
2. The mean flow velocities in the columns were designed to be quite similar to those in the "real" aquifer (between 1 and $1.5 \text{ m}\cdot\text{d}^{-1}$). However, due to the radial flow, the velocity in the aquifer decreases with the distance from the infiltration basin, by orders of magnitude (In Eq. 6.10 the flow decreases as a function of r^2 , where r is the radial distance from the basin). Moreover, preferential flow path within the aquifer may result in different water ages at any distance from the basin. Finally, the large heterogeneity in the hydrological conductivity and the flow velocity in the aquifer results in high dispersion as compared to that in the columns. Thus, the effluents recovered in the wells reflects a wide-scale average of the geochemical processes that occur along the flow paths, while the experimental outflow solutions are the product of a homogeneous system.

In order to compare between the experiments and the field data, it is necessary to convert the sampling date to the number of pore volumes of effluents that passed through the

aquifer since the onset of operation. Given that the residence time of the effluent in the aquifer is about 1 year, it follows that one pore volume passes through the active aquifer over this time period. Thus, the number of years since onset of effluent recharge represents the number of pore volume that passed through the active aquifer.

The significant cation exchange observed during the first pore volume flow in the experiments (stage I, Fig. 6.6) was not observed in the aquifer. Nevertheless, such exchange most probably did take place therein but was unnoticed because the temporal sampling resolution was low relative to the appearance of the cation breakthrough at the production wells, and because the dispersion in the aquifer was quite large. In the Soreq infiltration basin, however, the frequent sampling and the low dispersion (the observation well was located right at the center of the basin) enabled observing the cation exchange and the accompanying breakthrough curves at the onset of effluent recharge (Vengosh and Keren, 1996).

Na^+ adsorption and attainment of sediment-water equilibrium was a rapid process in the aquifer as observed under the Soreq infiltration basin (Idelovitch and Michail, 1984) in agreement with the results of the column experiments (that reached equilibrium within 5 pore volumes, see Figs. 6.2-6.6). Under the Yavne-2 infiltration basin, however, Na^+ appears to behave similarly to Cl^- and SO_4^{2-} (Figs. 6.11B, 6.12B). Since Na^+ is not a conservative element in the system, this suggests that it was adsorbed and equilibrated with the aquifer sediments during a very short time that was missed by the low temporal sampling resolution. Indeed, the later desorption of the Na^+ from the aquifer sediments in response to its decrease in the RE (see section 6.5.2 above), implies that Na^+ did adsorb onto the sediments and reached equilibrium at an earlier time. The reason that Na^+ breakthrough was not observed about two years after the onset of infiltration in Yavne-2 (equivalent to 2 pore volumes) but happened much earlier (probably within several months) is that the aquifer's CEC is 1/10 than the CEC of the sediments in the columns.

The retardation times of Mg^{2+} and K^+ are much larger than that of Na^+ (e.g. Stumm, 1992, and column experiments of this study, Figs. 6.2-6.5). This is the reason that despite the low sampling resolution, the increase of Mg^{2+} and K^+ toward equilibrium was clearly visible in Yavne-2 wells (Figs. 6.11C, 6.12C).

The retardation factor of K^+ in the Shafdan aquifer ($^KR_{SAT}$) as estimated from the field observations was 2 (section 6.5, Fig. 6.13), i.e., 1/10 than the ^KR measured in the column experiments ($^KR_{exp} = 20$). The same 1/10 ratio between the field and the experimental retardation factors was found also for Mg^{2+} ($^{Mg}R_{SAT} = 1.2 - 4.2$ versus $^{Mg}R_{exp} = 30$). These results imply that the CEC of the aquifer sediments is lower by an order of magnitude than that of the experimental column sediment. This indicates that adsorption in the aquifer is less significant than its role in the columns.

Since the aquifer is comprised mainly of calcareous sandstone, the Ca^{2+} concentrations in the aquifer are controlled by the carbonate system. Generally, Ca^{2+} concentrations in the outflow solution of the columns as well as in the production wells are determined by $CaCO_3$ dissolution and are higher than those in the RE by 1-2 $meq \cdot L^{-1}$ (Figs. 6.2-6.5, 6.11B, 6.12B). The Ca^{2+} concentrations in the outflow solutions of the columns (4.5-5 $meq \cdot L^{-1}$) are a somewhat lower than those in the aquifer (5-5.5 $meq \cdot L^{-1}$). The Ca^{2+} concentrations in the aquifer reflect saturation with respect to $CaCO_3$, while the Ca^{2+} in the outflow solutions of the columns are below their saturation level. Equilibrium was reached during the long residence time of water in the aquifer while the short residence time in the experimental columns (few hours up to 5 days) was too short to reach calcite saturation.

No field evidence was found either for Ca^{2+} desorption due to cation exchange in the first stage of the effluents recharge or for later Ca^{2+} adsorption (during the period that Na^+ desorption was observed in the aquifer). These processes most probably do occur in the aquifer, but are masked by the dominant process of $CaCO_3$ dissolution. Ca^{2+} desorption due to cation exchange was observed however in the Soreq infiltration basin during the first stage of the Shafdan SAT operation (Idelovitch and Michail, 1984). A complete dissolution of the sedimentary $CaCO_3$ occurred in column experiment EXP 5 after 940 pore volumes (section 6.3.2). Accordingly, it will take the RE at minimum 1000 y to dissolve all the carbonate in the Shafdan SAT system.

In summary, the results of the experiments provide a better understanding of the main geochemical process, cation exchange and $CaCO_3$ dissolution, which occur in the aquifer. The use of the red-brown sand in the column experiments ($CEC = 4.4 meq \cdot (100 g \text{ sediment})^{-1}$) rather than the more abundant calcareous sandstone in the aquifer enabled following the main processes and estimating a maximum adsorption potential within the

aquifer. The CEC of the bulk aquifer however, was found to be 1/10 than that of the experimental column sediment.

6.7 Summary

Both the experimental and field observations indicate that water-rock interactions alter the chemical composition of the effluents within the aquifer towards equilibrium. The column experiments show that the initial stage of artificial effluents recharge includes massive adsorption of Na^+ , K^+ and Mg^{2+} and desorption of Ca^{2+} . Field evidence for cation exchange includes the retardation of K^+ and Mg^{2+} and later, the desorption of Na^+ accompanied with adsorption of Mg^{2+} in response to change in RE composition.

In all column experiments, the initial solution that exited the columns was significantly depleted in Na^+ , K^+ and Mg^{2+} and enriched in Ca^{2+} compared to the inflowing 'artificial effluents'. Thereafter, Na_{out}^+ , K_{out}^+ and Mg_{out}^{2+} gradually increased while the Ca_{out}^{2+} decreased. Na^+ was the first to achieve equilibrium (attained the original inflow concentration), within 5 pore volumes, while K^+ and Mg^{2+} continued to exchange with Ca^{2+} over 20 and 30 pore volumes, respectively. This chromatographic behavior is due to the different affinities of the cations to the adsorption sites - longer duration of exchange representing greater affinity.

The Ca^{2+} concentrations in all production wells as well as in the outflow solution of the columns are higher by 1-2 $\text{meq}\cdot\text{L}^{-1}$ as compared to those in the RE due to CaCO_3 dissolution. Full dissolution of the available CaCO_3 in the aquifer rocks is expected to occur in the SAT system after a minimum time of 1000 y of continues operation.

The CEC of the red-brown sand used in the columns was determined by three independent methods to be $4.4 \pm 0.4 \text{ meq}\cdot(100 \text{ g sediment})^{-1}$. Ca^{2+} is the most abundant cation in the CEC, occupying about 90% of the adsorption sites in the pristine surface sediments and about 60% of the sites after equilibration with 'artificial effluents'. Mg^{2+} , the second most abundant cation, occupied about 20% of the adsorption sites in the column experiments. The monovalent cations, Na^+ and K^+ , are the least abundant, occupying < 10% each.

The CEC of the aquifer sediments is estimated to be 1/10 than that of the red-brown sand used in the columns, and hence it shows quantitatively less cation exchange. This is clearly demonstrated by the lower retardation factors of K^+ and Mg^{2+} in the aquifer (2 and 1.2-4.2) compared to those in the experiments (20 and 30 for K and Mg, respectively).

Chapter 7

Breakthrough behavior of reduced manganese in a sandy aquifer under suboxic conditions

7.1 Introduction

Mn^{2+} in aquatic environments is generally not a conservative element. The Mn^{2+} mobility is affected by several reactions: oxidation-reduction, adsorption-desorption and precipitation-dissolution (Morgan 2000). The mobility of Mn^{2+} is strongly affected by changes in the oxidation state within the aquifer (Stumm and Morgan 1981; Maynard 1983; Appelo and Postma 1996; Morel and Hering 1993). Under aerobic conditions Mn^{2+} may oxidize and precipitate as insoluble Mn-oxides such as MnO_2 and MnOOH . Under suboxic or anaerobic conditions the mobilization of Mn^{2+} may be retarded due to adsorption onto the aquifer sediments, mainly to clay minerals and organic matter (Appelo and Postma 1996; Flogeac et al. 2005), and/or precipitate as MnCO_3 if the carbonate content and pH conditions are appropriate (Garrels and Christ 1965; Maynard 1983). Since some of these processes are relatively slow, their kinetics impact significantly on the Mn geochemistry (Hem 1981; Maynard 1983; Stumm and Morgan 1981; Morgan 2000, 2005).

The mobilization of Mn in aquifers due to recharge of organic rich water have been the focus of several field and laboratory studies (Jacobs et al. 1988; Von Gunten et al. 1991;

Matsunaga et al. 1993; Bourg and Bertin 1993, 1994; Thomas et al. 1994; Ludvigsen et al. 1998; Petrunice et al. 2005). These studies emphasize the importance of the microbial reduction of Mn-oxides as the mechanism that drives Mn mobilization within the aquifer. Petrunice et al. 2005 suggested that cation exchange is another main process controlling Mn concentration in groundwater.

As described in Chapter 5, high Mn^{2+} concentrations first appeared in the groundwater under Yavne-2 SAT system of the Shafdan about 12 years after its operation first began (Halperin et al., 2003). This late Mn appearance occurred even though no apparent change in the redox conditions of the effluents or reclaimed water was observed. Given that the residence time of the water within the SAT system is no more than a year, this Mn retardation within the aquifer required an explanation.

In order to identify and quantify the processes that dictate the mobilization of reduced Mn^{2+} in the sandy aquifer of the Shafdan under suboxic conditions, columns laboratory experiments were conducted. The columns were filled with undisturbed red-brown sand from the Shafdan area. The experiments were conducted with solutions similar in composition to that of the Shafdan recharged effluents but with variable Mn^{2+} content. Suboxic conditions were maintained by continuously flushing nitrogen gas to the input solution container. It should be noted that the experiments did not include reduction of Mn-oxides as a source of Mn^{2+} . Rather reduced Mn^{2+} was supplied at constant concentration by the experimental solution which simulated the recharged 'artificial effluents'. The suboxic environment of the experiments precludes oxidation of the Mn^{2+} .

The present chapter deals with the processes that dictated the breakthrough behavior of reduced manganese under suboxic conditions. The experimental results are analyzed and evaluated using both an analytical and a numerical model. These models show that adsorption is the main process controlling Mn^{2+} mobilization while MnCO_3 precipitation may decrease the final Mn^{2+} concentration in the effluents under steady state conditions. Adsorption rates are shown to be orders of magnitude higher than those of precipitation. Finally, a rough estimation of the Mn amount that may be removed by adsorption onto the aquifer sediments in the SAT system of the Shafdan is discussed.

7.2 Solute transport modeling

A 1-D mass-balance equation for a solute that is mobilized in an aquifer is described by the general equation:

$$\left(\frac{\partial C}{\partial t} \right)_x = T_t \pm R_t \quad (7.1)$$

where, C - solute concentration; T - transport term; and R - reaction term. The $\pm$ denotes that the reaction may either produce or consume the particular solute and the subscripts x and t denote the distance and time, respectively. All solutes are transported by two mechanisms, advection - transport with the moving water, and diffusion - transport due to a concentration gradient. In the aquifer, the diffusion term is described by dispersion, which is larger than molecular diffusion due to the flow pattern in the porous medium (Scheidegger, 1954).

If adsorption is the sole reaction that takes place, an analytical model may be used to describe the solute breakthrough curve. The analytical model assumes instantaneous adsorption, a constant distribution coefficient and does not include mineral precipitation or dissolution. In order to account also for the impact of mineral precipitation and the kinetic effect of both adsorption and precipitation, a numerical model is required. The analytical and numerical models used in the present study are described below.

7.2.1 Analytical model

The overall rate of change in a solute concentration due to its transport and reaction of adsorption/desorption can be described as (Appelo and Postma, 1996):

$$\left(\frac{\partial C}{\partial t} \right)_x = D \cdot \left(\frac{\partial^2 C}{\partial x^2} \right)_t - v \cdot \left(\frac{\partial C}{\partial x} \right)_t - \left(\frac{\partial q}{\partial t} \right)_x \quad (7.2)$$

where, C -concentration of the cation in pore solution ($\text{meq} \cdot \text{L}^{-1}$), D - dispersion coefficient ($\text{cm}^2 \cdot \text{h}^{-1}$), v - flow velocity of pore solution ($\text{cm} \cdot \text{h}^{-1}$), q - concentration of the cation adsorbed on the solid ($\text{meq} \cdot \text{L}^{-1}$), $q = K_d \cdot C$

Replacing $\left(\frac{\partial q}{\partial t} \right)$ by $K_d \cdot \left(\frac{\partial C}{\partial t} \right)$ and further rearrangement of Eq. 7.2 yields:

$$(1 + K_d) \cdot \left(\frac{\partial C}{\partial t} \right)_x = D \cdot \left(\frac{\partial^2 C}{\partial x^2} \right)_t - v \cdot \left(\frac{\partial C}{\partial x} \right)_t \quad (7.3)$$

The coefficient $(1 + K_d)$ is the retardation factor, R , which decreases the apparent dispersion coefficient and the flow velocity. The solution of Eq. 7.3 for $x=L$, the length of an experimental column, yields the so called breakthrough curve (modified from Van Genuchten and Parker, 1984):

$$C(L, t) = C_0 + \frac{C_{in} - C_0}{2} \cdot \left(\operatorname{erfc} \left[\frac{L - \frac{v \cdot t}{(1+K_d)}}{\sqrt{\frac{4 \cdot D \cdot t}{(1+K_d)}}} \right] + \exp \left[\frac{L \cdot v}{D} \right] \cdot \operatorname{erfc} \left[\frac{L + \frac{v \cdot t}{(1+K_d)}}{\sqrt{\frac{4 \cdot D \cdot t}{(1+K_d)}}} \right] \right) \quad (7.4)$$

where, C_0 - Initial concentration of the cation in the column ($\text{meq} \cdot L^{-1}$); C_{in} - Concentration of the cation in the inflow solution ($\text{meq} \cdot L^{-1}$).

The boundary conditions for solving Eq. 7.4 are: C_{in} , the concentration at the column entrance is constant; and the forward dispersion at $x=L$ is zero (due to flow of water out of the column).

7.2.2 Numerical model

The numerical model includes a transport term and two relevant reaction terms, all of which are discussed individually in the following sections.

7.2.2.1 The transport term

A 1-D mass-balance equation for a solute that is affected only by transport in pore water is described by the dispersion-advection equation (Bear, 1972):

$$\left(\frac{\partial C}{\partial t} \right)_x = T_t = D \cdot \left(\frac{\partial^2 C}{\partial x^2} \right)_t - v \cdot \left(\frac{\partial C}{\partial x} \right)_t \quad (7.5)$$

where, C - solute concentration ($\text{meq} \cdot L^{-1}$); D - dispersion coefficient ($\text{cm}^2 \cdot \text{h}^{-1}$); and v - flow velocity ($\text{cm} \cdot \text{h}^{-1}$).

For numerical solution of Eq. 7.5, the dispersion term can be approximated by finite differences as (see for example Anderson and Woessner, 1992):

$$D \cdot \left(\frac{\partial^2 C}{\partial x^2} \right)_t = D \cdot \frac{C_{x-\Delta x}^{t-\Delta t} - 2 \cdot C_x^{t-\Delta t} + C_{x+\Delta x}^{t-\Delta t}}{(\Delta x)^2} \quad (7.6)$$

and the advection term expressed as:

$$v \cdot \left(\frac{\partial C}{\partial x} \right)_t = v \cdot \frac{C_{x+\Delta x}^{t-\Delta t} - C_{x-\Delta x}^{t-\Delta t}}{2 \cdot \Delta x} \quad (7.7)$$

where, Δt - time increment; and Δx - distance increment.

Accordingly, the change in concentration as a function of time at any location x can be approximated by finite differences by substituting Eq. 7.6 and Eq. 7.7, into Eq. 7.5:

$$\begin{aligned} \frac{\Delta C}{\Delta t} \Big|_x &= \frac{C_x^t - C_x^{t-\Delta t}}{\Delta t} = \frac{D}{(\Delta x)^2} \cdot \left(C_{x-\Delta x}^{t-\Delta t} - 2 \cdot C_x^{t-\Delta t} + C_{x+\Delta x}^{t-\Delta t} \right) - \\ &\quad \frac{v}{2 \cdot \Delta x} \cdot \left(C_{x+\Delta x}^{t-\Delta t} - C_{x-\Delta x}^{t-\Delta t} \right) \end{aligned} \quad (7.8)$$

Rearrangement of this equation results in a numerical solution for advection and dispersion:

$$C_x^t = C_x^{t-\Delta t} + \frac{D \cdot \Delta t}{(\Delta x)^2} \cdot \left(C_{x-\Delta x}^{t-\Delta t} - 2 \cdot C_x^{t-\Delta t} + C_{x+\Delta x}^{t-\Delta t} \right) - \frac{v \cdot \Delta t}{2 \cdot \Delta x} \cdot \left(C_{x+\Delta x}^{t-\Delta t} - C_{x-\Delta x}^{t-\Delta t} \right) \quad (7.9)$$

7.2.2.2 The reaction terms

The reaction term in Eq. 7.1 represents any geochemical process relevant to the solute concentration during the flow. In the case of Mn^{2+} mobilization in suboxic environment, two reactions should be considered, adsorption/desorption and precipitation/dissolution of MnCO_3 phase. This phase is hereafter assumed to be the mineral rhodochrosite¹. The numerical expressions developed for these reactions are discussed below. The pε–pH conditions prevailing in the Shafdan aquifer and in the columns fall within the stability fields of MnCO_3 and Mn^{2+} and well outside the stability fields of the Mn-oxide phases (Fig. 1.3B). Therefore, precipitation of Mn-oxides is not included in the numerical model.

Adsorption/desorption

It is assumed that the adsorption/desorption reaction is pseudo-linear. Therefore, the reaction rate is linearly dependent on the reaction rate coefficient and the distance from

¹The only thermodynamic data available for a MnCO_3 phase is that of rhodochrosite. This data is required for the construction of the precipitation term in the advection-dispersion-reaction model.

adsorption saturation concentration (the concentration of the cation in the water when adsorption/desorption equilibrium is attained), as expressed by the following equation:

$$\frac{\Delta C}{\Delta t}|_x = k_a \cdot (C_{ads_sat} - C_{x,t}) \quad (7.10)$$

where, k_a - adsorption rate coefficient (h^{-1}); and C_{ads_sat} - the calculated cation concentration at adsorption/desorption equilibrium ($\text{meq} \cdot \text{L}^{-1}$).

A positive difference ($C_{ads_sat} - C_{x,t}$) induces desorption and a negative difference induces adsorption. The larger the absolute value of the difference ($C_{ads_sat} - C_{x,t}$) the faster the reaction.

C_{ads_sat} is calculated from the total amount of the exchangeable cation in a defined unit volume, $M_{total} = M_{solid} + M_{porewater}$ as follows:

$$M_{total} = A \cdot \Delta x \cdot \varepsilon \cdot C_{x,t} + A \cdot \Delta x \cdot \varepsilon \cdot q_{x,t} = A \cdot \Delta x \cdot \varepsilon \cdot (C_{x,t} + q_{x,t}) \quad (7.11)$$

where, A - cross section area (cm^2); ε - porosity; and q - adsorbed cation concentration on solid in terms of pore water volume ($\text{meq} \cdot \text{L}^{-1}$). The value of q is converted from units of mass per kg sediment to units of mass per L of pore water by multiplying the adsorbed concentration, $s \left(\text{mass} \cdot (\text{kg sediment})^{-1} \right)$, by the bulk density of the sediment, $\rho_b \left((\text{g dry sediment}) \cdot (\text{mL sediment})^{-1} \right)$, and dividing by the porosity, ε (Appelo and Postma, 1996).

At equilibrium, the total amount of the exchangeable cation M_{total}^{eq} , is:

$$M_{total}^{eq} = A \cdot \Delta x \cdot \varepsilon \cdot (C_{ads_sat} + K_d \cdot C_{ads_sat}) \quad (7.12)$$

where, K_d is the distribution coefficient of the cation between solid and pore water as expressed by the equation:

$$K_d = \frac{q_{ads_sat}}{C_{ads_sat}} \quad (7.13)$$

Substituting Eq. 7.11 in Eq. 7.12 yields:

$$A \cdot \Delta x \cdot \varepsilon \cdot (C_{x,t} + q_{x,t}) = A \cdot \Delta x \cdot \varepsilon \cdot (C_{ads_sat} + K_d \cdot C_{ads_sat}) \quad (7.14)$$

Rearranging Eq. 7.14 yields an expression for the C_{ads_sat} :

$$C_{ads_sat} = \frac{C_{x,t} + q_{x,t}}{1 + K_d} \quad (7.15)$$

Substituting Eq. 7.15 in Eq. 7.10 and rearranging yields a numerical solution for adsorption/desorption term:

$$C_x^t = C_x^{t-\Delta t} + k_a \cdot \Delta t \cdot \left(\left(\frac{C_x^{t-\Delta t} + q_x^{t-\Delta t}}{1 + K_d} \right) - C_x^{t-\Delta t} \right) \quad (7.16)$$

where $q_x^{t-\Delta t}$ is calculated by a corresponding equation written for the solid. In this equation, the adsorbed cation concentration on the solid at time t is calculated by subtracting the second term in Eq. 7.16 (the concentration change in pore water) from the solid's previous (at time $t - \Delta t$) cation concentration. This equation is:

$$q_x^t = q_x^{t-\Delta t} - k_a \cdot \Delta t \cdot \left(\left(\frac{C_x^{t-\Delta t} + q_x^{t-\Delta t}}{1 + K_d} \right) - C_x^{t-\Delta t} \right) \quad (7.17)$$

Rhodochrosite precipitation/dissolution

Similarly to the case of the adsorption reaction above, the rhodochrosite (MnCO_3) precipitation/dissolution reaction is assumed to be pseudo-linear. Therefore, the reaction rate is linearly dependent on the reaction rate coefficient and the distance from rhodochrosite saturation concentration:

$$\frac{\Delta C}{\Delta t} \Big|_x = k_p \cdot (C_{rho_sat} - C_{x,t}) \quad (7.18)$$

where, k_p - rhodochrosite (MnCO_3) precipitation rate coefficient; and $C_{rho_sat} - \text{Mn}^{2+}$ concentration at saturation with rhodochrosite ($\text{meq} \cdot \text{L}^{-1}$).

The C_{rho_sat} is determined by the apparent solubility product as follows:

$$[\text{Mn}^{2+}] = \frac{K'_{sp_rho}}{[\text{CO}_3^{2-}]} \quad (7.19)$$

where, K'_{sp_rho} - apparent solubility product of rhodochrosite (the thermodynamic solubility product divided by the product of the activity coefficients of Mn^{2+} and CO_3^{2-}); and $[\text{Mn}^{2+}]$, $[\text{CO}_3^{2-}]$ - Mn^{2+} and CO_3^{2-} concentrations ($\text{mol} \cdot \text{L}^{-1}$) at equilibrium with

rhodochrosite. $[\text{CO}_3^{2-}]$ was calculated from its relation to alkalinity and pH:

$$[\text{CO}_3^{2-}] = \frac{K_2 \cdot (\text{ALK} - [\text{OH}^-] + [\text{H}^+])}{([\text{H}^+] + 2 \cdot K_2)} \quad (7.20)$$

where, K_2 - The second equilibrium constant of carbonic acid (between HCO_3^- and CO_3^{2-}) for freshwater (Stumm and Morgan, 1981); ALK - carbonate alkalinity ($\text{eq} \cdot \text{L}^{-1}$), and $[\text{OH}^-]$, $[\text{H}^+]$ - hydroxide and hydrogen ion concentrations ($\text{mol} \cdot \text{L}^{-1}$).

Substituting Eq. 7.20 into Eq. 7.19 yields the Mn saturation concentration with respect to rhodochrosite given the solution's ALK and pH:

$$C_{\text{rho_sat}} = \frac{K'_{\text{sp_rho}} \cdot 2 \cdot 1000}{\left(\frac{K_2 \cdot (\text{ALK} - \text{OH}^- + \text{H}^+)}{(\text{H}^+ + 2 \cdot K_2)} \right)} \quad (7.21)$$

The factor of $2 \cdot 1000$ was used to convert $[\text{Mn}^{2+}]$ from molar to mili-equivalent concentration units in order to fit Eq. 7.18.

Accordingly, the numerical solution for rhodochrosite precipitation/dissolution rate is:

$$C_x^t = C_x^{t-\Delta t} + k_p \cdot \Delta t \cdot \left(\left(\frac{K'_{\text{sp_rho}} \cdot 2 \cdot 1000}{\left(\frac{K_2 \cdot (\text{ALK} - \text{OH}^- + \text{H}^+)}{(\text{H}^+ + 2 \cdot K_2)} \right)} \right) - C_x^{t-\Delta t} \right) \quad (7.22)$$

7.2.2.3 The overall transport-reaction equation

The overall transport-reaction equation is the sum of all terms discussed above:

$$\begin{aligned} C_x^t = C_x^{t-\Delta t} &+ \frac{D \cdot \Delta t}{(\Delta x)^2} \cdot \left(C_{x-\Delta x}^{t-\Delta t} - 2 \cdot C_x^{t-\Delta t} + C_{x+\Delta x}^{t-\Delta t} \right) - \frac{\nu \cdot \Delta t}{2 \cdot \Delta x} \cdot \left(C_{x+\Delta x}^{t-\Delta t} - C_{x-\Delta x}^{t-\Delta t} \right) + \\ &k_a \cdot \Delta t \cdot \left(\left(\frac{C_x^{t-\Delta t} + q_x^{t-\Delta t}}{1 + K_d} \right) - C_x^{t-\Delta t} \right) + k_p \cdot \Delta t \cdot \left(\left(\frac{K'_{\text{sp_rho}} \cdot 2 \cdot 1000}{\left(\frac{K_2 \cdot (\text{ALK} - \text{OH}^- + \text{H}^+)}{(\text{H}^+ + 2 \cdot K_2)} \right)} \right) - C_x^{t-\Delta t} \right) \end{aligned} \quad (7.23)$$

This equation together with Eq. 7.17 (the adsorbed Mn) was used to calculate the breakthrough curves of Mn^{2+} .

7.3 Methods

Laboratory column experiments (details in section 6.2) were designed to simulate the mobilization of Mn^{2+} during flow of groundwater in a sandy aquifer under suboxic conditions. The breakthrough curves of Mn^{2+} have been simulated with the analytical and the numerical models presented above. The numerical model calculations were carried out using the "MATLAB" code, version 7.0 (model codes are provided in Appendix 15).

7.4 Experiments results

The breakthrough curves of Mn^{2+} in column experiments with different inflow Mn^{2+} concentrations, Mn_{in}^{2+} , are presented in Fig. 7.1 (data in Appendices 8-10, 12). In all experiments Mn^{2+} first appearance in the column outflow solution occurred after about 40-50 pore volumes. This was long after the concentrations of the major cations have stabilized on their equilibrium or steady state values (Chapter 6). After its appearance, Mn^{2+} outflow concentration, Mn_{out}^{2+} , increased and stabilized. The final Mn^{2+} concentration varied as a function of the Mn_{in}^{2+} : in the 'low Mn^{2+} concentration experiment' (EXP 3) the final concentration was similar to that of the inflow concentration; in the experiments with higher Mn^{2+} concentrations the final Mn^{2+} stabilized on a value lower than that of the inflow concentrations. The higher the Mn^{2+} inflow concentration was, the sharper its increase in the outflow concentration was. Accordingly, the higher the Mn^{2+} inflow concentration was, the earlier the Mn^{2+} breakthrough point, defined as half the steady state concentration, was reached. In the high Mn^{2+} concentration experiments (EXP 2 and EXP 4), the increase in Mn_{out}^{2+} before the breakthrough inflection point is sharper than its increase after the inflection point.

The above observations indicate that during the flow in the columns, Mn^{2+} is significantly retarded. Adsorption on column solids is the main process causing this retardation. The non-symmetrical (around the inflection point) shape of the Mn^{2+} breakthrough curves was most probably caused by precipitation of MnCO_3 (rhodochrosite). When approaching rhodochrosite saturation, the increase in Mn^{2+} "slowed down" as reflected in the upper parts (above inflection point) of the breakthrough curves. The high Mn^{2+} concentration experiments stabilized on Mn_{out}^{2+} lower than the Mn_{in}^{2+} due to rhodochrosite precipitation. In the 'low Mn^{2+} concentration experiment', however,

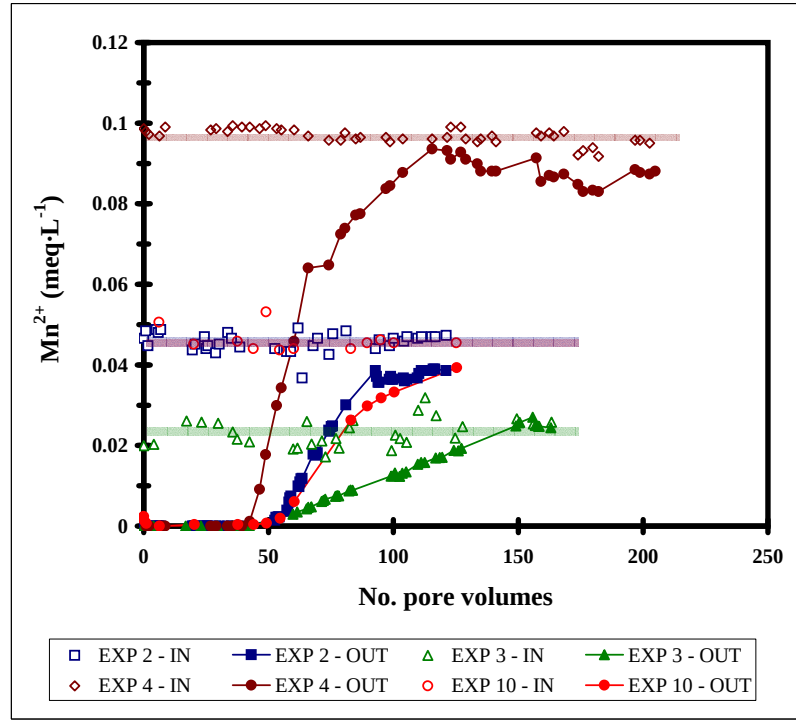


FIGURE 7.1: Breakthrough curves of Mn^{2+} in four experiments with different inflow concentrations.

Mn_{out}^{2+} stabilized exactly on the Mn_{in}^{2+} , indicating that the solution is undersaturated with respect to rhodochrosite. The suboxic conditions maintained in the experimental system, rule out the possibility that precipitation of Mn-oxide is responsible for the observed "lower" outflow Mn^{2+} steady state concentrations. Analytical and numerical simulations of these processes are presented below.

7.4.1 The apparent distribution coefficient of Mn between effluents and Shafdan aquifer sediments

The distribution coefficient of Mn, ${}^{Mn}K_d$, is the ratio of adsorbed Mn(II) to dissolved Mn^{2+} concentrations at equilibrium (per unit volume of porewater). It is however easier to calculate an apparent distribution coefficient, ${}^{Mn}K'_d$, for the experimental column as follows:

$${}^{Mn}K'_d = \frac{q_{total}}{C_{out}} \quad (7.24)$$

where, q_{total} - the steady state concentration of the solid phase Mn(II) ($\text{mg} \cdot \text{L}^{-1}$), and C_{out} - the steady state concentration of Mn^{2+} in the outflow solution ($\text{mg} \cdot \text{L}^{-1}$). The

q_{total} is the difference between the total amount of Mn^{2+} that entered the column and the total amount of Mn^{2+} that exited the column when steady state was first attained, divided by the total pore volume. Thus, in the experiments in which rhodochrosite precipitated (EXP 2 and EXP 4, see above), q_{total} includes both the adsorbed $Mn(II)$, $q_{adsorbed}$ and the Mn-carbonate phase, q_{MnCO_3} :

$$q_{total} = q_{adsorbed} + q_{MnCO_3} \quad (7.25)$$

and hence the apparent $^{Mn}K'_d$ is:

$$^{Mn}K'_d = ^{Mn}K_d + \frac{q_{MnCO_3}}{C_{out}} \quad (7.26)$$

Accordingly, $^{Mn}K'_d$ will be an overestimation of $^{Mn}K_d$ when rhodochrosite precipitation occurs. The parameters used in the calculations and the calculated $^{Mn}K'_d$ are presented in Table 7.1 (for estimates of q_{MnCO_3} and $^{Mn}K_d$, see section 7.6 below).

The apparent distribution coefficient calculated for the 'high Mn^{2+} concentration experiment' ($^{Mn}K'_d = 76$) is significantly lower than those of the lower Mn^{2+} concentration experiments ($^{Mn}K'_d$ values about 90). This suggests that the shape of the apparent sorption isotherm (q_{total}/C_{out}) is convex and not linear in the examined range of Mn^{2+} concentrations. Precipitation of rhodochrosite in the 'high and moderate Mn^{2+} concentration experiments' imply that $^{Mn}K'_d > ^{Mn}K_d$. Accordingly, the shape of the true sorption isotherm ($q_{adsorbed}/C_{out}$) should be even more convex than the apparent one. As discussed below, such a convex sorption isotherm was obtained from the analytical model (section 7.6).

TABLE 7.1: Apparent Mn^{2+} distribution coefficients ($^{Mn}K'_d$) calculated from the solid phase and the solute concentrations in the three experiments. The parameters used for the calculations are listed in the Table. All parameters were rounded to 2 significant digits after calculation.

Parameter Inflow Mn^{2+} concentration	Sign (units)	EXP 3 Low	EXP 2 Moderate	EXP 4 High
Apparent distribution coefficient of Mn^{2+}	$^{Mn}K'_d$	91	93	76
Steady state concentration of the solid phase Mn(II)	$s_{total} (\text{mg} \cdot \text{kg}^{-1})$	17	27	43
Solute concentration in outflow solution at equilibrium	$C_{out} (\text{mg} \cdot \text{L}^{-1})$	0.65	1.0	2.4
Bulk density	$\rho_b (g \cdot \text{mL}^{-1})$	1.5	1.5	1.5
Porosity	ε	0.42	0.42	0.36
Steady state concentration of the solid phase Mn(II)	$q_{total} (\text{mg} \cdot \text{L}^{-1})$	59	95	180

7.4.2 Flow velocity and Mn^{2+} mobilization

One of the experiments (EXP 10) was conducted with varying flow velocity in order to evaluate the effect of the rate of transport on the Mn^{2+} controlling processes (Fig. 7.2, Appendix 12). After attainment of steady state (Fig. 7.1), the flow velocity was lowered by a factor of 5 in 2 gradual steps (from $4 \text{ mL} \cdot \text{h}^{-1}$ to $0.8 \text{ mL} \cdot \text{h}^{-1}$); Later, the flow was increased by a factor of 4 in 4 gradual steps (from $4 \text{ mL} \cdot \text{h}^{-1}$ to $14.3 \text{ mL} \cdot \text{h}^{-1}$); the flow was stopped for 4.5 days between step 3 and step 4 (Fig. 7.2A). During the initial stage of EXP 10 (stage I) Mn^{2+} (Fig. 7.2C) and Ca^{2+} (Fig. 7.2B) concentrations stabilized on their steady state concentrations (lower and higher than their inflow concentrations due to rhodochrosite precipitation and carbonate dissolution, respectively). During the rest of the experiment Ca^{2+} only varied slightly whereas Mn^{2+} changed substantially. During the low flow velocity stage (stage II) Mn^{2+} decreased while in the high flow velocity stage (stage III) it increased up to the inflow concentration. These results suggest that MnCO_3 precipitation in the column is a very slow process. This is corroborated by the significant decrease in Mn^{2+} concentration that followed the 4.5 days of zero flow at the end of stage III. As expected, during this time Ca^{2+} concentration increased towards its

thermodynamic equilibrium value. It should be noted that at stage IV, which followed the zero flow period, the trends of Ca^{2+} and Mn^{2+} remained as before.

In summary, EXP 10 proves that a solid Mn phase (MnCO_3) precipitated in the experimental column and that the rate of this reaction is slow.

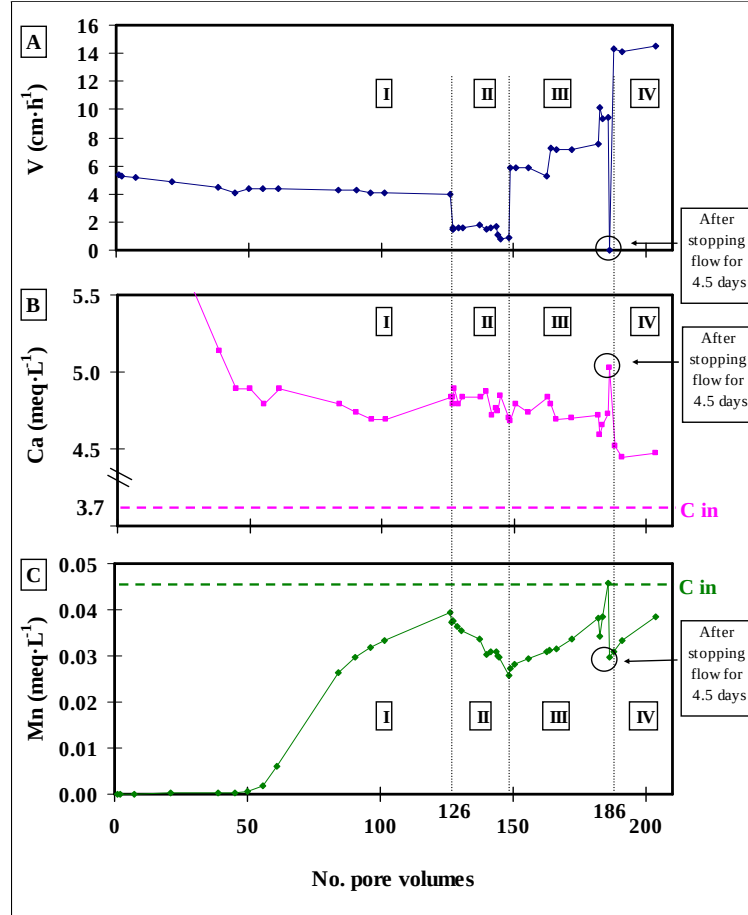


FIGURE 7.2: Flow velocity (A), Ca^{2+} concentration (B), and Mn^{2+} concentration (C) versus number of pore volumes in EXP 10. At 126 pore volumes, after attaining steady state (stage I) the flow velocity decreased in 2 steps to $0.8 \text{ ml} \cdot \text{h}^{-1}$ (stage II), followed by an increase in 4 steps to $14.3 \text{ ml} \cdot \text{h}^{-1}$ (stage III). During the increases, between step 3 and step 4, the flow was stopped for 4.5 days (marked by the circles).

7.5 Analytical model

Analytical solutions for the Mn^{2+} breakthrough curves in the experiments are presented in Figs. 7.3 - 7.6. The model is presented in Eq. 7.4 and the parameters used for the calculations are listed in Table 7.2. This model, however, assumes instantaneous

adsorption, a constant $^{Mn}K_d$, and does not include rhodochrosite precipitation. The $^{Mn}K_d$ values were varied between the simulation runs to obtain the best fit with the observed Mn^{2+} breakthrough curve (Figs. 7.3 - 7.6). The $^{Mn}K_d$ values that best fit the data are listed in Table 7.2

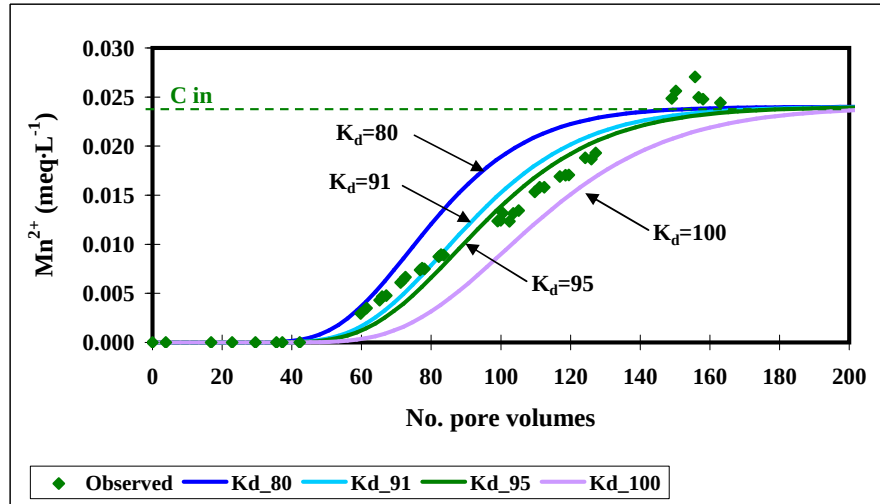


FIGURE 7.3: Experimental data showing the Mn^{2+} breakthrough for the 'low concentration experiment' (EXP-3). Simulations of the breakthrough curves calculated by the analytical model (Eq. 7.4) for different values of $^{Mn}K_d$ (marked by the arrows) are represented by the solid lines. The line for $^{Mn}K_d=95$ (solid green line) represents the best fit with the experimental data.

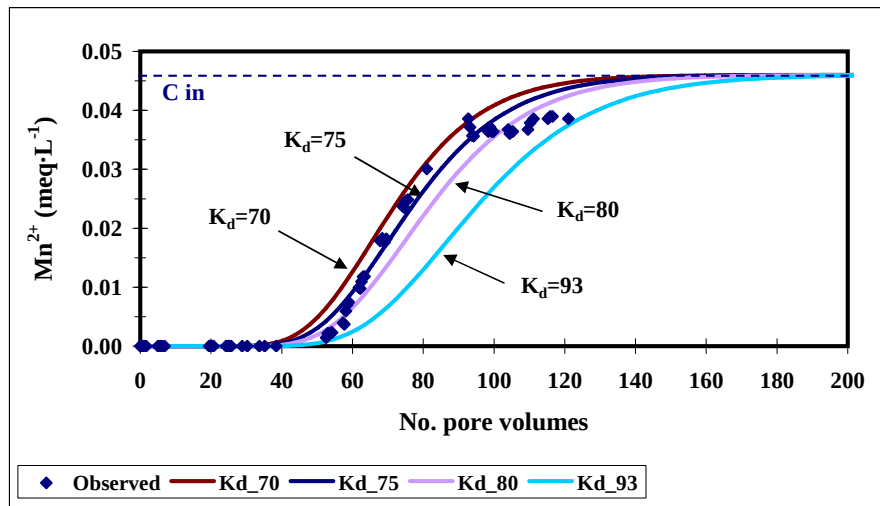


FIGURE 7.4: Experimental data showing the Mn^{2+} breakthrough for the 'moderate concentration experiment' (EXP-2). Simulations of the breakthrough curves calculated by the analytical model (Eq. 7.4) for different values of $^{Mn}K_d$ (marked by the arrows) are represented by the solid lines. The line for $^{Mn}K_d=75$ (solid blue line) represents the best fit with the experimental data.

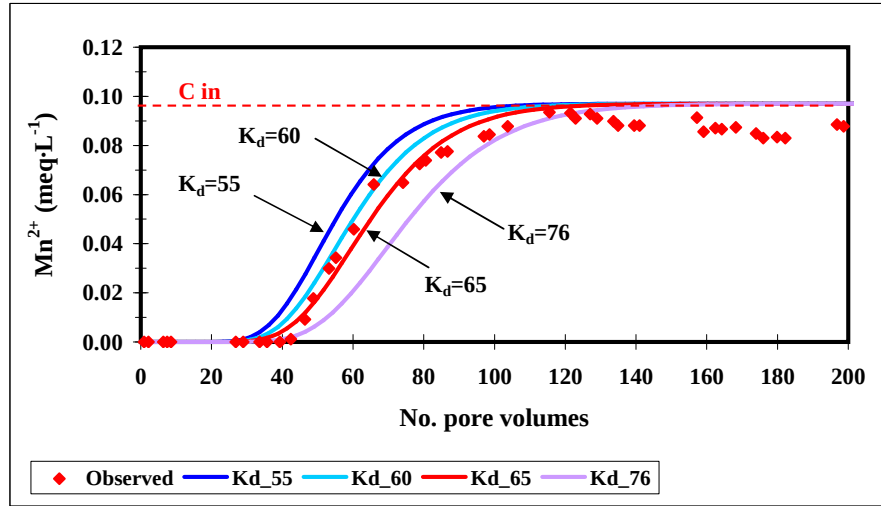


FIGURE 7.5: Experimental data showing the Mn^{2+} breakthrough for the 'high concentration experiment' (EXP-4). Simulations of the breakthrough curves calculated by the analytical model (Eq. 7.4) for different values of $^{\text{Mn}}K_d$ (marked by the arrows) are represented by the solid lines. The line for $^{\text{Mn}}K_d=65$ (solid red line) represents the best fit with the experimental data.

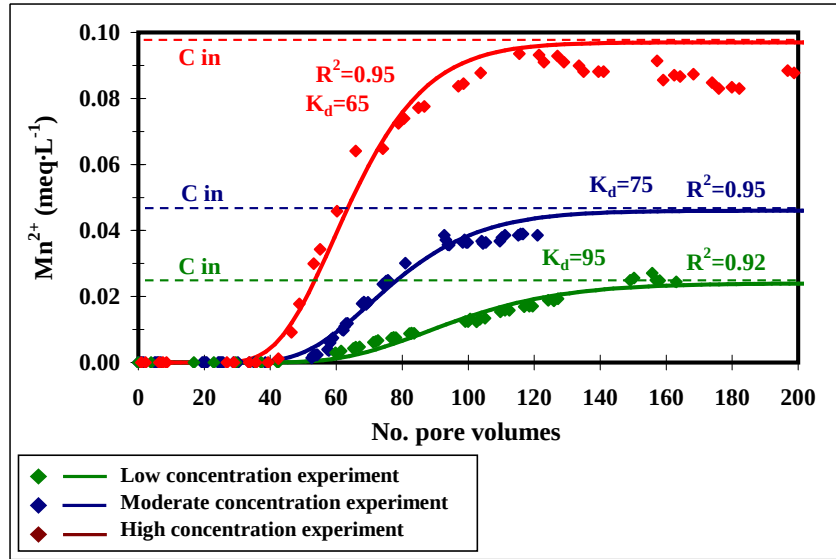


FIGURE 7.6: Comparison of the three Mn^{2+} column experiments shown in Figs. 7.3-7.5 showing that the $^{\text{Mn}}K_d$ obtained from the best fit of the **analytical** breakthrough curves decreases with increasing Mn^{2+} inflow concentrations.

The good correlation between the experimental data and the model results indicates that advection, dispersion and adsorption are the main processes controlling Mn^{2+} mobilization. It should be noted however that while the simulated Mn^{2+} attains the exact Mn^{2+} inflow concentrations in all experiments, in two of the experiments (EXP 2 and EXP 4), the actual data stabilizes on lower Mn^{2+} concentrations. The two experiments were

those with moderate Mn^{2+} and high Mn^{2+} inflow concentrations (Fig. 7.6). The discrepancy between the calculated and the observed results may stem from precipitation of MnCO_3 within the experimental column, which is not accounted for in the analytical model. Adding a MnCO_3 precipitation term to the numerical model presented below (section 7.6), successfully resolves this discrepancy.

The results of the analytical model indicate that the higher the Mn^{2+} inflow concentration, the lower the $^{Mn}K_d$, in agreement with the apparent distribution coefficient calculated from the Mn mass-balance for the experimental data (section 7.4.1). The values of $^{Mn}K_d$ obtained in both calculations are very similar for the 'low Mn^{2+} concentration experiment' (EXP 3). In the other two experiments the $^{Mn}K'_d$ values calculated from the Mn mass-balance for the experimental data were higher than $^{Mn}K_d$ values calculated by the analytical model. This indicates that the solid phase Mn(II) used in the mass-balance calculations contained also MnCO_3 that was precipitated during the experiments and not only adsorbed Mn(II). The amount of MnCO_3 , q_{MnCO_3} , that precipitated in the column was calculated using Eq. 7.26, from the apparent $^{Mn}K'_d$ values calculated from the Mn mass-balance and the real $^{Mn}K_d$ values calculated by the analytical model. The obtained q_{MnCO_3} values are 18.4 and 26.6 $\text{mg} \cdot \text{L}^{-1}$ in EXP 2 and EXP 4, respectively. This means that MnCO_3 precipitation accounts for a deficit of ca. 1/5 of the total Mn removed by the experimental column from the beginning up to the establishment of steady state outflow concentration (while 4/5 of the Mn was removed by adsorption on aquifer sediments).

TABLE 7.2: Descriptions, symbols, units and values of parameters used in the simulations with the analytical model (Ana in column 3) and the numerical model (Num in column 3). The detailed explanation of the numerical model is given in section 7.6 below.

Parameter	Sign (units)	Model	EXP 3	EXP 2	EXP 4
Initial concentration in column	C_0 (meq $\cdot$ L ⁻¹)	Ana+Num	0	0	0
Concentration of introducing solution	C_{in} (meq $\cdot$ L ⁻¹)	Ana+Num	0.024	0.046	0.097
Flow velocity	v (cm $\cdot$ h ⁻¹)	Ana+Num	5.2	4.2	5.1
Dispersivity	α (cm)	Ana+Num	0.8 ^a	0.8 ^a	0.8 ^a
Dispersion coefficient ($D = \alpha \cdot v$)	D (cm ² $\cdot$ h ⁻¹)	Ana+Num	4.2	3.4	4.1
Distribution coefficient	$^{Mn}K_d$	Ana+Num	95	75	65
Time increment	Δt (h)	Ana	10	10	10
		Num	0.005	0.005	0.005
Distance increment	Δx (cm)	Num	0.5	0.5	0.5
Adsorption rate coefficient	k_a (h ⁻¹)	Num	10	200	200
MnCO ₃ precipitation rate coefficient	k_p (h ⁻¹)	Num	0.05	0.05	0.03
Alkalinity	ALK (eq $\cdot$ L ⁻¹)	Num	0.005	0.005	0.005
pH	pH	Num	6.8	6.8	6.8
MnCO ₃ apparent solubility product	K'_{sp-rho}	Num	$2.24 \cdot 10^{-11}$ ^b	$2.24 \cdot 10^{-11}$ ^b	$2.24 \cdot 10^{-11}$ ^b
Equilibrium constant between HCO ₃ ⁻ and CO ₃ ²⁻	K_2	Num	$10^{-10.25}$ ^c	$10^{-10.25}$ ^c	$10^{-10.25}$ ^c

^a value taken from similar experiments made by Russak et al.,2008 (personal communication).

^b from [Lide, 1991](#), p. 8-43.

^c from [Stumm and Morgan, 1981](#), p. 176.

7.5.1 Mn^{2+} sorption isotherm on aquifer rocks

A sorption isotherm describes the distribution of a substance between a solid phase and the aqueous phase that is in contact with that solid. It is used for describing and predicting mobilization by groundwater of substances with affinity to the solid phase (Limousin et al., 2007). The simplest description of the distribution of a parameter between the solid and the aqueous phases is the linear sorption isotherm: $q = K_d \cdot C$ (where $q = q_{\text{adsorbed}}$ and C are the adsorbed and dissolved concentrations, respectively, and K_d is the distribution coefficient). A linear isotherm means that K_d is constant or that the solid saturation concentration may reach infinity. Such a model is generally used for describing the behavior of trace components (Appelo and Postma, 1996). The more general case is when the concentration of a particular component in the solid phase is limited by saturation (Limousin et al., 2007). In this case, q is not a linear function of C but has a convex shape (q approaches the saturation concentration) and the distribution coefficient ($K_d = q/C$) decreases as a function of solute concentration. Indeed, the shape of a q_{Mn} versus C_{Mn} plot for the data obtained in the three column experiments seems to be convex (Fig. 7.7). The best fit to these experimental data was obtained by the *Langmuir sorption isotherm* (Langmuir, 1918):

$$q = q_{\text{max}} \cdot \frac{L \cdot C}{1 + L \cdot C} \quad (7.27)$$

assuming that the column saturation concentration for Mn^{2+} (q_{max}) is about three fold the maximum concentration used in the experiments ($q_{\text{max}} = 18 \text{ meq} \cdot \text{L}^{-1}$). The steepness constant (dimensionless) L for those conditions is 5.5. According to Eq. 7.27, ${}^{\text{Mn}}K_d = \frac{q}{C} = \frac{q_{\text{max}}}{C + \frac{1}{L}}$ where q and C are Mn^{2+} concentrations. It is clear that in the range of the Mn^{2+} concentrations used in the column, $q \ll q_{\text{max}}$ and hence the ${}^{\text{Mn}}K_d$ does not vary much.

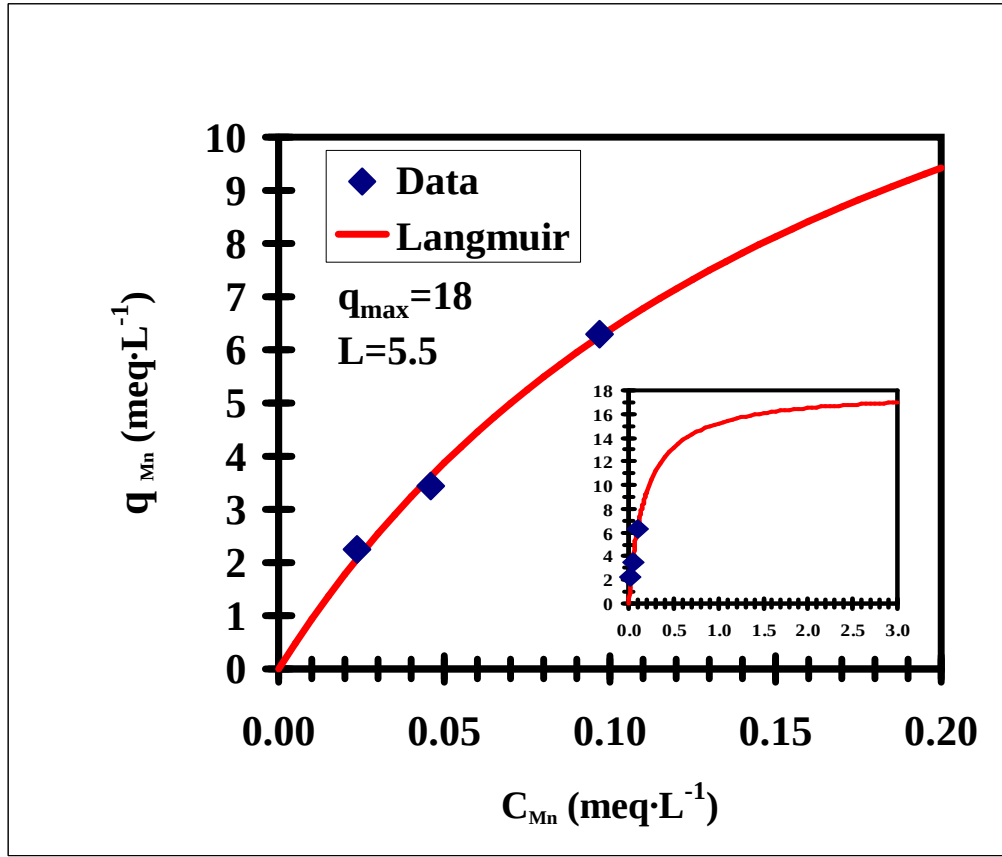


FIGURE 7.7: Mn^{2+} concentration in the solids (q_{Mn}) versus its concentration in the liquid (C_{Mn}) for the three column experiments described in Fig. 7.6. The best fit between the Langmuir sorption isotherm and the experimental data was obtained for $q_{\text{max}}=18$ and $L=5.5$.

7.6 Numerical model

The numerical model (Eq. 7.23) enables calculating the Mn^{2+} breakthrough curve as a function of all processes identified in this study (transport, adsorption and MnCO_3 precipitation). The schematic flow chart of the model, the computer code (MATLAB), and the parameters used are presented Fig. 7.8, Appendix 15 and Table 7.2, respectively. Simultaneous calculation of the Mn^{2+} adsorbed on the solid (Eq. 7.17) was conducted for completing the Mn mass-balance for the experimental column.

The time and distance increments (Δt and Δx , respectively) used in the model were chosen to be $\Delta t = 0.005$ h and $\Delta x = 0.5$ cm, in order to minimize numerical dispersion. The conditions for selecting these increments were: 1. $v \cdot \Delta t < \Delta x$ and 2. $D \cdot \Delta t < (\Delta x)^2$. The $^{Mn}K_d$ values used to model each of the experiments were those calculated by the analytical model to best fit the data (Eq. 7.4 and Section 7.5). The adsorption and

precipitation rate coefficients, k_a and k_p , were obtained by best fitting of the numerical model runs with the experimental results.

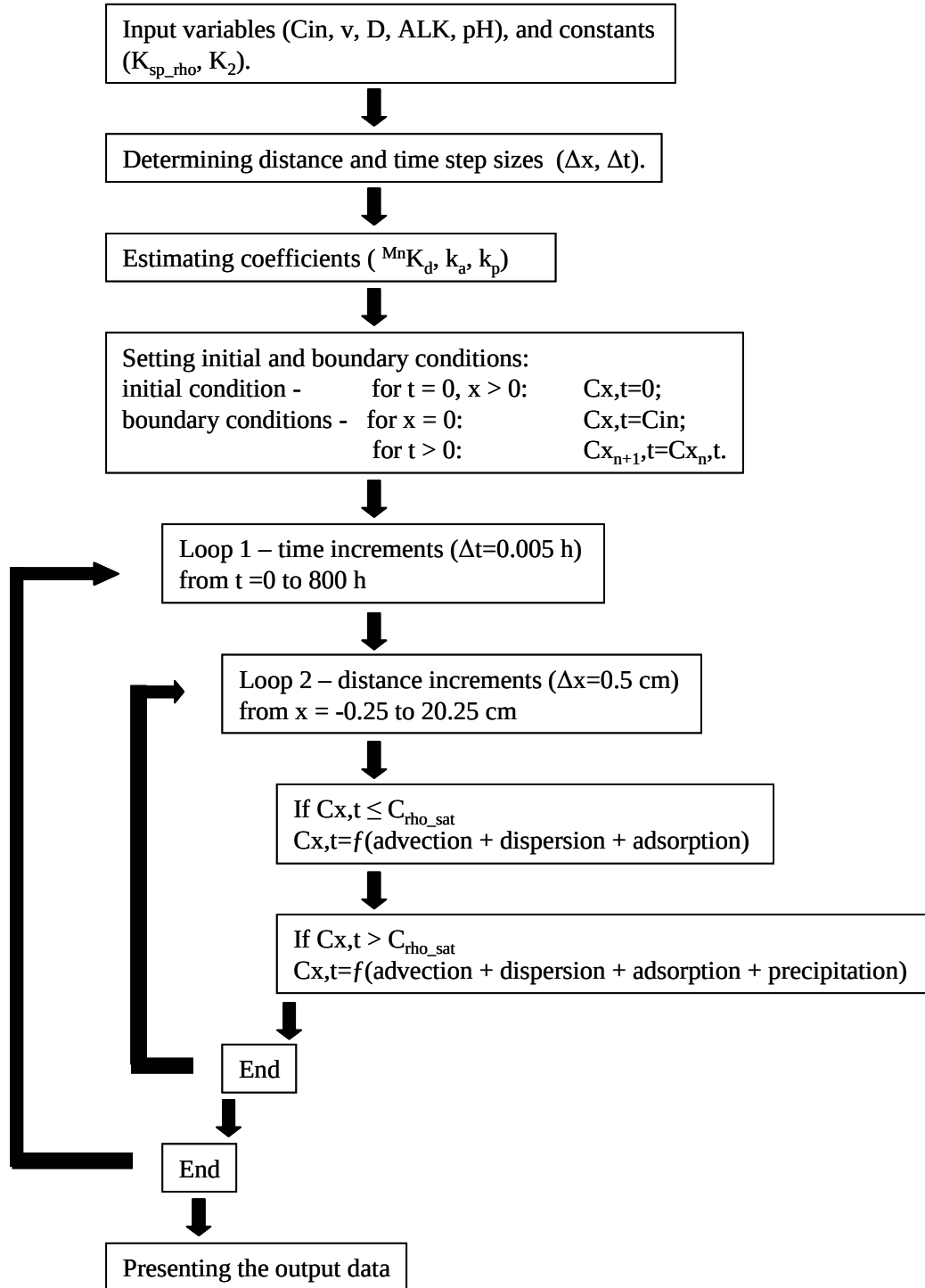


FIGURE 7.8: Flow diagram of the numerical model progress.

The initial and boundary conditions for t and x used for solving the numerical model were:

1. $C_x^0 = 0$ for $t = 0$ at any x from $x = 1 \cdot \Delta x$ to $x = (N + 1) \cdot \Delta x$.
2. $C_0^t = C_{in}^t$ for $x = 0$ at any t .
3. $C_{N+1}^t = C_N^t = C_{out}^t$ for $x = (N + 1) \cdot \Delta x$ at any t .

where, t and x notations are similar to those in Eq. 7.23; N is the number of cells (each of length $= \Delta x$) in the experimental columns. The model includes two additional virtual cells to facilitate the calculations, one before the entrance to the column, at $x = 0$, representing the solution that enters the column (the inflow solution with concentration C_{in}^t) and the second after the exit of the column, at $x = (N + 1) \cdot \Delta x$, representing the solution at the column outlet (the outflow solution with concentration C_{out}^t).

The numerical model runs (Figs 7.9, 7.10) show that the transport (advection and dispersion) and adsorption terms control mainly the shape and retardation of Mn^{2+} breakthrough (Fig. 7.9). The numerical model reproduces very well the experimental breakthrough curves for the different inflow concentrations (Fig. 7.10). The higher the inflow concentration is, the earlier the appearance of Mn^{2+} at the outflow and the sharper the rise of the breakthrough curve (Figs. 7.10, 7.11).

In order to obtain steady state outflow concentrations of Mn^{2+} that are lower than the inflow concentrations (as observed in experiments with high Mn^{2+} inflow concentrations) a $MnCO_3$ precipitation term is required (Fig. 7.9). In the numerical model simulations a K_{sp-rho} value of $2.24 \cdot 10^{-11}$ (Lide, 1991) was used. The published K_{sp-rho} values range over three orders of magnitude, from $3.09 \cdot 10^{-13}$ (Jensen et al., 2002) to $3.39 \cdot 10^{-10}$ (McBeath et al., 1998). When the highest value is used in the model, the solution does not reach saturation with respect to rhodochrosite whereas using the lowest value requires decreasing the precipitation rate coefficient (Fig. 7.12).

The travel time of the Mn^{2+} front (represented by the number of pore volumes to reach the breakthrough inflection point, Fig. 7.10) indicates that the retardation factor is negatively correlated with the Mn^{2+} inflow concentration. The higher the Mn^{2+} inflow concentration is, the earlier appears the Mn^{2+} front. This phenomenon results from the observed decrease in $^{Mn}K_d$ with increasing Mn^{2+} inflow concentrations (the convex

shape of the Mn sorption isotherm, see section 7.5.1 above). As described in Chapter 5 above (see also Appelo and Postma, 1996), the retardation factor is defined by the ratio between the water flow velocity and the velocity of the Mn^{2+} , which is a function of $^{Mn}K_d$ according to the equation:

$$R = \frac{v}{v_{\text{Mn}^{2+}}} = 1 + ^{Mn}K_d \quad (7.28)$$

The expression $(1 + K_d)$ for the retardation factor follows directly from Eq. 7.3 above. When the water flow velocity in the experiments was kept constant, the retardation factor equaled the ratio between the travel time of the Mn^{2+} breakthrough inflection point and the travel time of any conservative parameter (e.g. Cl^-) that is affected only by transport. The appropriate retardation factors for the high, moderate and low Mn^{2+} concentration experiments were 65, 76 and 94, respectively (Figs. 7.9, 7.10). As mentioned above, this provides additional evidence to the convex shape of the Mn adsorption isotherm.

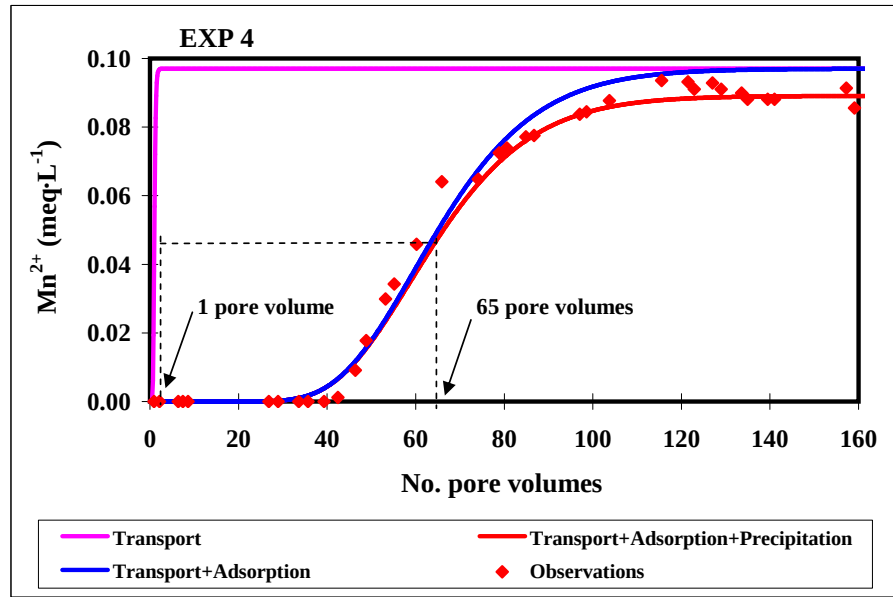


FIGURE 7.9: The numerical model run for the breakthrough curve of EXP 4, the 'high Mn^{2+} concentration experiment' (red diamonds). The different lines show the curve resulting from transport only (pink); transport and adsorption (blue); and the complete model including transport, adsorption, and MnCO_3 precipitation (red).

The fine tuning of the model to the experimental results was made by adjusting the rate coefficients of Mn^{2+} adsorption and MnCO_3 precipitation (k_a and k_p , respectively, see Eq. 7.23 and Table 7.2). Best fit with the experimental data was obtained for

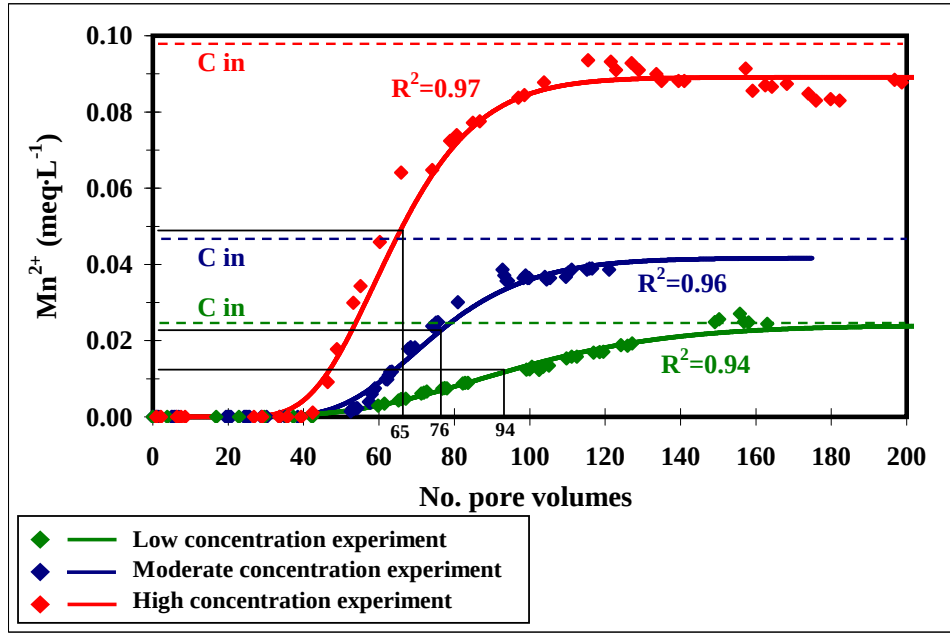


FIGURE 7.10: Experimental points and **numerical** model breakthrough curves of Mn^{2+} for different inflow concentrations.

$10 \leq k_a \leq 200 \text{ h}^{-1}$ (Fig. 7.13), while for $k_a = 1 \text{ h}^{-1}$ there is clearly no fit. For $k_a \geq 250 \text{ h}^{-1}$ the model 'exploded' and yielded negative Mn^{2+} values. The high adsorption rate coefficient (200 h^{-1}) provided the best fit for the 'moderate and high Mn^{2+} concentration experiments' (Figs. 7.13B, 7.13C) and the low k_a (10 h^{-1}) fitted best the results of the 'low Mn^{2+} concentration experiment' (Fig. 7.13A). The apparent dependence of k_a on Mn^{2+} concentration may indicate that the rate law for Mn adsorption is pseudo-linear. It should be noted that the value of 200 h^{-1} is the highest the model can run with before it crashes. It is therefore possible that the adsorption rate coefficient of 200 h^{-1} is in fact an underestimate and that the 'moderate and high Mn^{2+} concentration experiments' have different and higher rate coefficients.

The best fit to the experimental data yielded a MnCO_3 precipitation rate coefficient (k_p) of $0.03 - 0.05 \text{ h}^{-1}$, which is at least 3 orders of magnitude lower than the adsorption rate coefficient. This indicates that MnCO_3 precipitation rate is much slower than the Mn^{2+} adsorption rate.

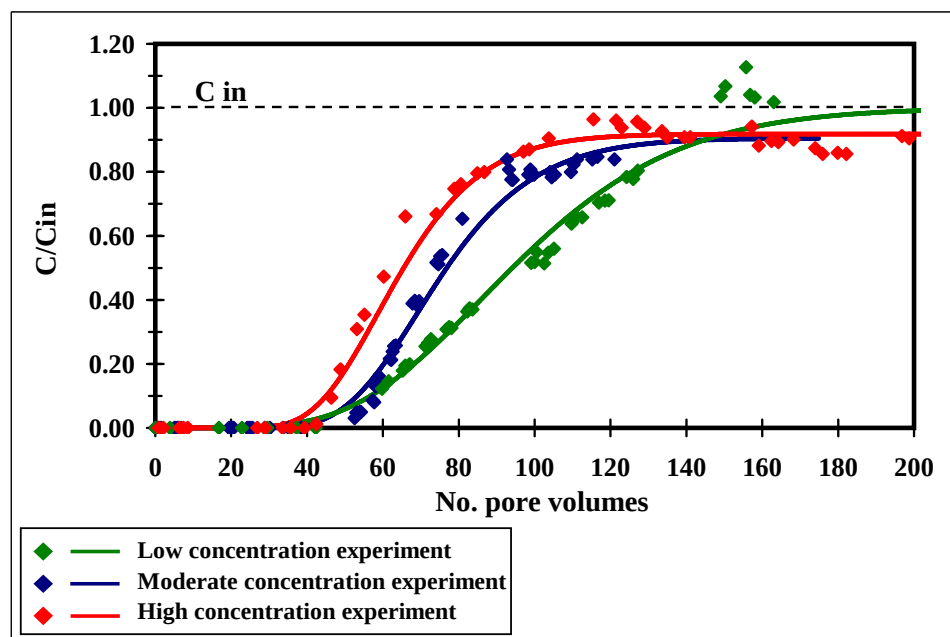


FIGURE 7.11: Experimental points and **numerical** model breakthrough curves of the Mn^{2+} concentration fractions for the different inflow concentrations.

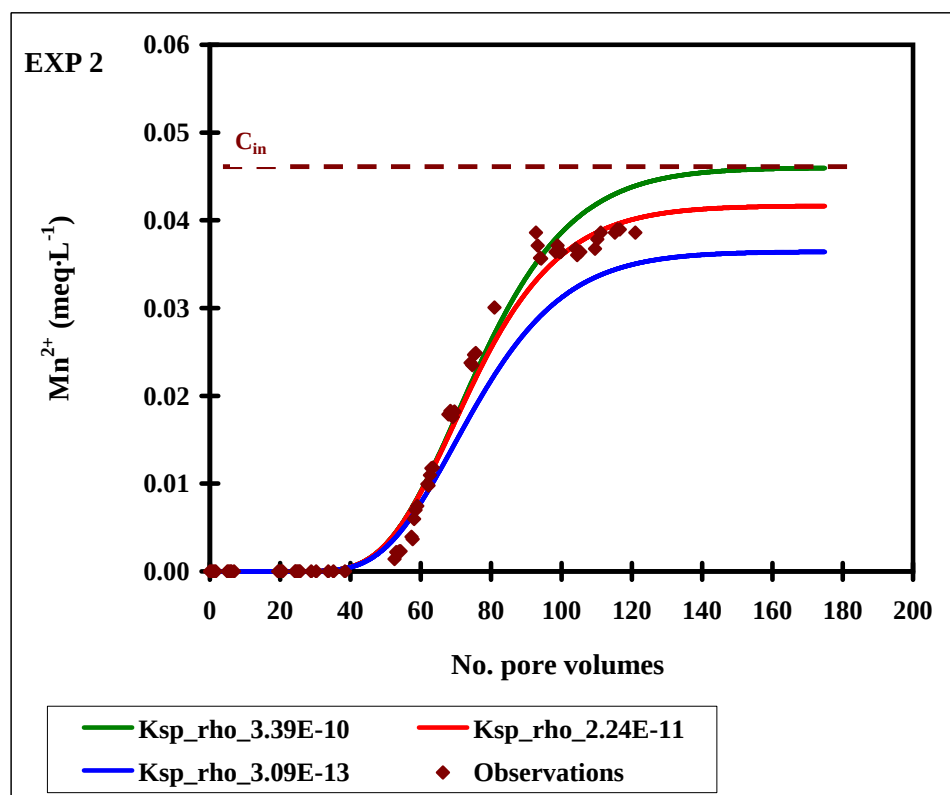


FIGURE 7.12: Numerical model runs for the breakthrough curve of EXP 2 using different values of rhodochrosite solubility product (K_{sp-rho}).

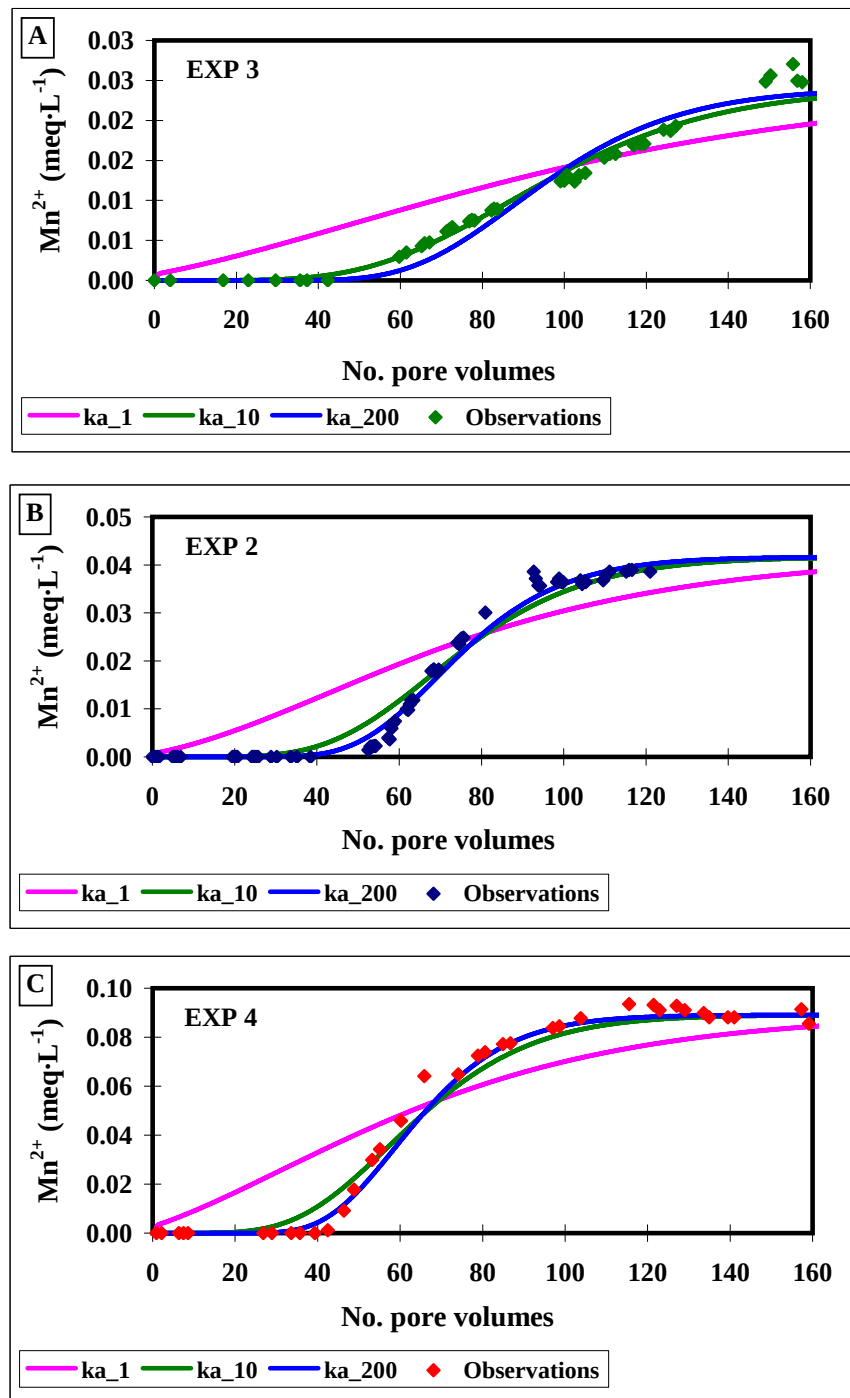


FIGURE 7.13: Best fit of the adsorption coefficient rate to the experimental breakthrough curve of: (A) the 'low Mn^{2+} concentration experiment' (EXP 3); (B) the 'moderate Mn^{2+} concentration experiment' (EXP 2); and (C) the 'high Mn^{2+} concentration experiment' (EXP 4).

7.7 The potential of the Shafdan aquifer rocks to adsorb manganese

As discussed in section 6.6, the Mn^{2+} adsorption capacity (MAC) of the sandy sediment used in the simulation experiments was much higher (probably by a factor of 10) than the MAC of the Shafdan aquifer calcareous sandstones. In spite of the different characteristics, the results of the column simulation experiments were used to constrain potential MAC of the Shafdan's Yavne-2 SAT system.

Applying the Mn sorption isotherm (Fig. 7.7, and section 7.5.1) as described by Eq. 7.27, the Mn adsorbed concentrations (q), as a function of the Mn^{2+} dissolved in the aquifer (C) is expressed by the equation:

$$q \text{ (meq} \cdot L^{-1}) = \frac{18}{1 + \frac{0.18}{C \text{ (meq} \cdot L^{-1})}} \quad (7.29)$$

The total amount of Mn(II) that may adsorb onto Yavne-2 aquifer sediments (Mn_{ads_aqu}) when in equilibrium with dissolved Mn^{2+} (Eq. 7.29) can be calculated using the following equation:

$$Mn_{ads_aqu} \text{ (Ton)} = q \text{ (eq} \cdot m^{-3}) \cdot \bar{V}_{aquifer} \text{ (m}^3) \cdot \frac{1}{10} \cdot \frac{54.94}{2} \text{ (gMn} \cdot eq^{-1}) \cdot 10^{-6} \text{ (Ton} \cdot g^{-1}) \quad (7.30)$$

where the coefficient 1/10 is the MAC of aquifer sediments to MAC of experimental column sediments ratio (section 6.6); and the volume of water in the aquifer is calculated by: $\bar{V}_{aquifer} = \pi \cdot r^2 \cdot Z \cdot \varepsilon$, where, r - radius of Yavne-2 SAT system containing the adsorbed Mn(II) (500 m); Z - thickness of the aquifer (60 m); and ε - porosity (0.4).

The Mn_{ads_aqu} versus aquifer's C_{Mn} plot (Fig. 7.14) shows that the amounts of Mn(II) adsorbed in the Yavne-2 field are between 90 and 260 Ton (given Mn^{2+} concentrations in the groundwater between 0.02 and 0.07 meq $\cdot L^{-1}$). This value is much greater than the total amount of Mn^{2+} that was recharged into Yavne-2 field or the total amount of Mn recovered by the production wells (see Fig. 3, Chapter 5).

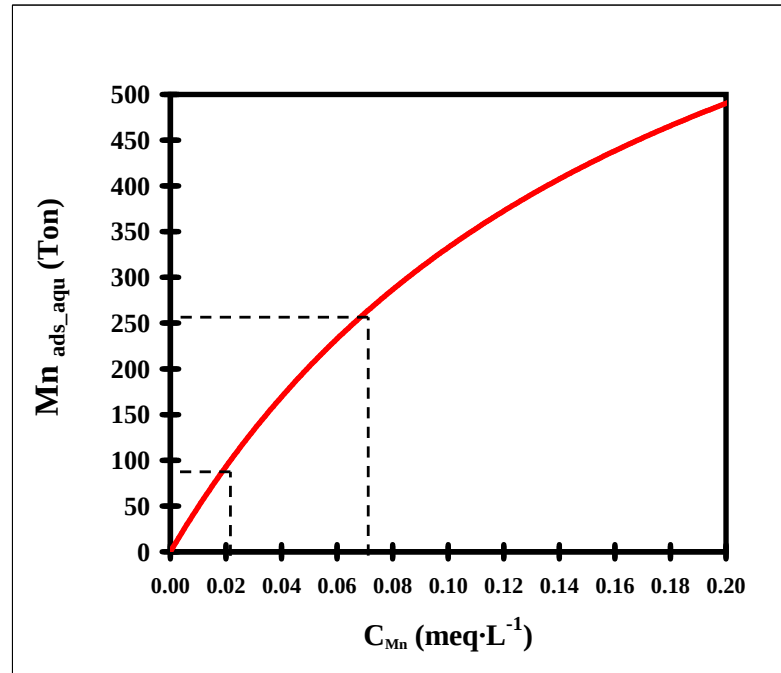


FIGURE 7.14: The amount of Mn(II) that may be adsorbed onto the aquifer sediments versus its concentration in groundwater (C_{Mn}), calculated by Eqs.7.29 and 7.30. The range between the dashed lines represents the expected amounts of adsorbed Mn(II) according to the observed dissolved Mn^{2+} concentrations within the aquifer.

7.8 Summary

The Mn^{2+} adsorption experiments conducted in this study were designed to follow the Mn^{2+} breakthrough behavior under suboxic conditions and different Mn^{2+} inflow concentrations. Analytical and numerical models that were fitted to the experimental data enabled identification and quantification of the processes controlling Mn mobilization in the columns and within the aquifer. The main conclusions are summarized below.

- Mn is retarded much longer than all major cations during the flow of water through sandy sediments under suboxic conditions. The first appearance of Mn^{2+} in the outflow solutions of the column occurred after water passage of 40-50 pore volumes.
- The Mn^{2+} outflow concentration stabilized on values similar or lower than that of the inflow solutions, depending on the Mn^{2+} inflow concentration.

- The higher the inflow Mn^{2+} concentration, the earlier the appearance of Mn^{2+} at the outflow solution and the sharper the rise of the breakthrough curve.
- The main process controlling the behavior of the Mn^{2+} breakthrough curves is adsorption of Mn(II) onto the aquifer sediments.
- The Mn sorption isotherm in the examined range of Mn^{2+} concentrations is convex and not linear, i.e. the higher the Mn^{2+} inflow concentration the lower the $^{Mn}K_d$ (calculated as q/C). The data were best described by the *Langmuir sorption isotherm* model: $q \text{ (meq} \cdot \text{L}^{-1}) = 18 \cdot \frac{5.5 \cdot C}{1 + 5.5 \cdot C}$, where $18 \cdot \text{meq} \cdot \text{L}^{-1}$ is the saturation concentration of the adsorbed Mn(II).
- Apparently, MnCO_3 (rhodochrosite) precipitation occurred in the high and moderate Mn^{2+} concentration experiments. In this case the Mn^{2+} outflow concentrations stabilized on values lower than those of the inflow solutions. By that time, out of the total Mn removed by the column, 1/5 was precipitated as MnCO_3 and 4/5 was removed by adsorption.
- The MnCO_3 precipitation rate coefficient ($k_p = 0.04 \text{ h}^{-1}$) is lower by at least 3 orders of magnitude than the adsorption rate coefficient (k_a between 10 h^{-1} and 200 h^{-1}). Thus, the kinetics of MnCO_3 precipitation is much slower than that of the adsorption, indicating that adsorption controls Mn^{2+} retardation.
- The total amount of Mn(II) adsorbed onto the Yavne-2 aquifer sediments is estimated to range between 90 and 260 Ton. This suggests that the total amount of the adsorbed Mn(II) is much larger than the total Mn^{2+} recharged in the infiltration basin or the total Mn recovered by the production wells.

Chapter 8

Summary and Conclusions

The present study deals with the aquatic geochemistry of Mn during the interaction of groundwater enriched in organic matter with calcareous-sandstone rocks. The site selected for the study was the Yavne-2 infiltration system, which is part of the larger soil aquifer treatment (SAT) system of the Shafdan plant. In the Shafdan SAT system, the calcareous-sandstone aquifer is recharged with treated effluents enriched in dissolved organic matter. The groundwater is being pumped for reuse in irrigation few hundred meters down stream of the Yavne-2 infiltration basin. The water rock interactions along the flow path of the groundwater are discussed and modeled, focusing on the processes controlling the Mn mobilization. The thesis is summarized with a conceptual model summarizing the geochemical evolution and Mn mobilization (Fig. 8.1).

Cation exchange and CaCO_3 dissolution are the main processes modifying the chemical composition of the effluents during their flow in the aquifer. This is deduced from the chemical composition of water collected in wells drilled into the aquifer and laboratory simulations with columns packed with Shafdan sediments. The main phenomena occurring during the initial stage of recharge with effluents are massive adsorption of Na^+ , K^+ and Mg^{2+} and desorption of Ca^{2+} . These continue until equilibrium and steady state are achieved. Slight changes in the composition of the recharged effluents (RE) result in additional cation exchange to reestablish equilibrium between the fluid and rock. For example, decrease in the Na^+ concentration in the RE of the Shafdan SAT system lead to Na^+ desorption from the sediments, accompanied by adsorption of Mg^{2+} and possibly also Ca^{2+} .

Ca^{2+} concentrations increase by 1-2 meq·L⁻¹ as compared to that in the RE in all production wells of Yavne-2 SAT system, as well as in the outflow solutions of the columns, reaching calcite saturation. This is due to CaCO_3 dissolution by the RE which is undersaturated with respect to calcite.

The pretreated effluents that recharge the aquifer are enriched in organic matter and ammonium, which oxidize almost completely (to CO_2 and nitrate) during the effluent infiltration through the vadose zone. The oxidation of organic matter and the nitrification processes consume the dissolved oxygen, causing suboxic conditions that facilitate reduction of sedimentary Mn-oxide and its mobilization as Mn^{2+} in the groundwater. Indeed, high Mn concentrations were found only in 100% wells where the DO concentration is $< 50 \mu\text{mol}\cdot\text{L}^{-1}$.

The Mn budget for the period from the onset of the Yavne-2 SAT system operation until 2004 indicates that during this period the aquifer rocks lost at least 8 Ton of Mn due to reduction of sedimentary Mn-oxides and Mn^{2+} mobilization with the groundwater. This loss is reflected in the low Mn (and Mn-oxides) content in the calcareous sandstones of the aquifer, below the water table, as compared to the concentrations in similar but pristine sediments that were not exposed to leaching by RE. On the other hand, the concentration of Mn in the infiltrating effluents within the vadose zone (0-9 m) and in the groundwater below the infiltration basin is low. These observations strongly suggest that most of the Mn is mobilized within the saturated zone of the aquifer and not in the vadose zone.

The recharge regime in the Yavne-2 infiltration basin and the RE composition remained constant since the onset of the basin operation. Therefore, and due to the rapid kinetics of Mn reduction, it is concluded that Mn reduction began soon after the onset of the Yavne-2 SAT operation (once the effluents replaced the freshwater in the aquifer) and that this process has been continuing at a constant rate as of that time. Yet, high Mn concentrations first appeared in the production wells around the infiltration basin only in the year 2000, about 12 years after the beginning of operation. The Mn retardation is attributed to massive adsorption of reduced Mn(II) onto the aquifer sediments, as simulated also in the columns.

The Mn sorption isotherm obtained from the column simulation runs, suggests that the total amount of Mn(II) adsorbed onto the Yavne-2 aquifer sediments ranges between 90

and 260 Ton. The experiments also verified that Mn retardation is much greater than that of all major cations during the flow of water through the sandy sediments under suboxic conditions. The Mn^{2+} breakthrough behavior is controlled by the adsorption capacity of Mn(II). Therefore, the higher the Mn^{2+} concentration in the inflow solution, the earlier it appears in the outflow solutions and the sharper is the rise of its breakthrough curve.

MnCO_3 ("rhodochrosite") precipitation sets the upper limit on Mn^{2+} concentration in the groundwater at high Mn^{2+} concentrations ($> 700 \mu\text{g}\cdot\text{L}^{-1}$ for $\text{ALK}=0.005 \text{ eq}\cdot\text{L}^{-1}$ and $\text{pH}=6.8$). A transport-reaction numerical model formulated in the present study suggests that the kinetics of MnCO_3 precipitation is much slower than that of the adsorption, indicating that the adsorption controls the Mn^{2+} retardation. The MnCO_3 precipitation rate coefficient ($k_p=0.04 \text{ h}^{-1}$) is lower by at least 3 orders of magnitude than the adsorption rate coefficient (k_a between 10 h^{-1} and 200 h^{-1}).

In summary, a front of high Mn^{2+} concentration advances in the direction of the groundwater flow within the calcareous-sandstone aquifer containing 100% effluents (Fig. 8.1A, B). It is expected that the Mn front will eventually reach the hydrologic trough around the basin, which contains a mixture of effluents and oxidized fresh groundwater. Mixing between these water types will result in oxidation and precipitation of Mn-oxides in the aquifer (Fig. 8.1C). Thus, groundwater pumped in wells located within the trough, which at present contains low levels of Mn, will remain so also in the future. Accordingly, the advance of the Mn front is expected to stop when it reaches the hydrologic trough. The mobilization of the Mn in the aquifer is expected to stop when all the labile sedimentary Mn content within the region of the 100% effluents will be consumed.

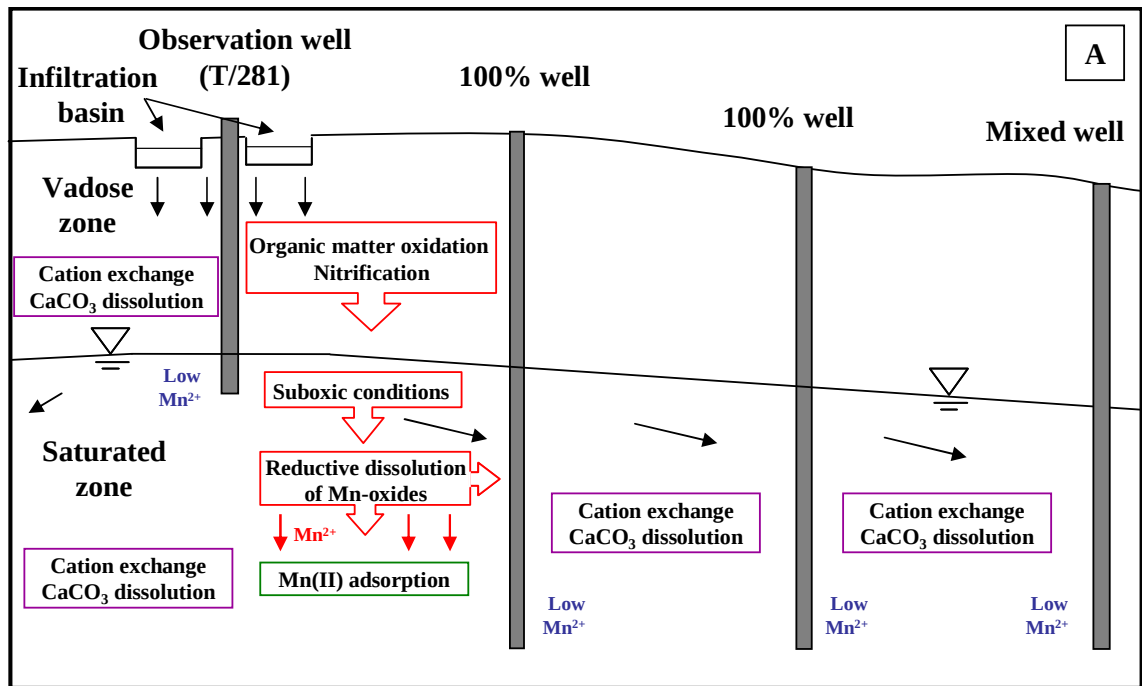
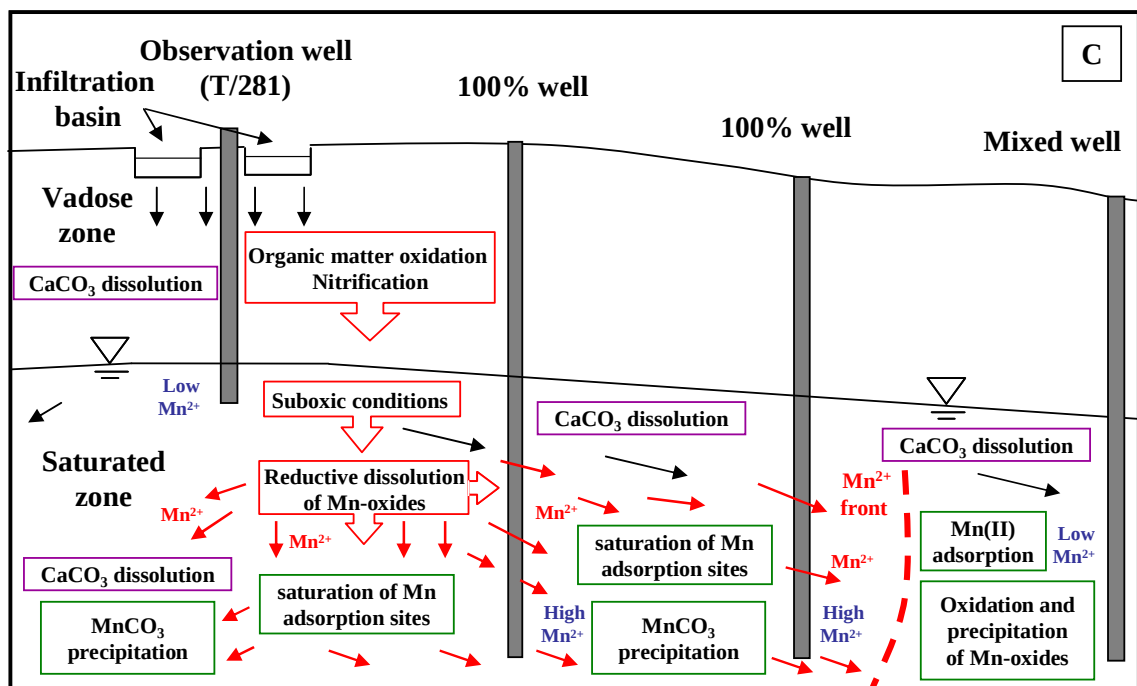
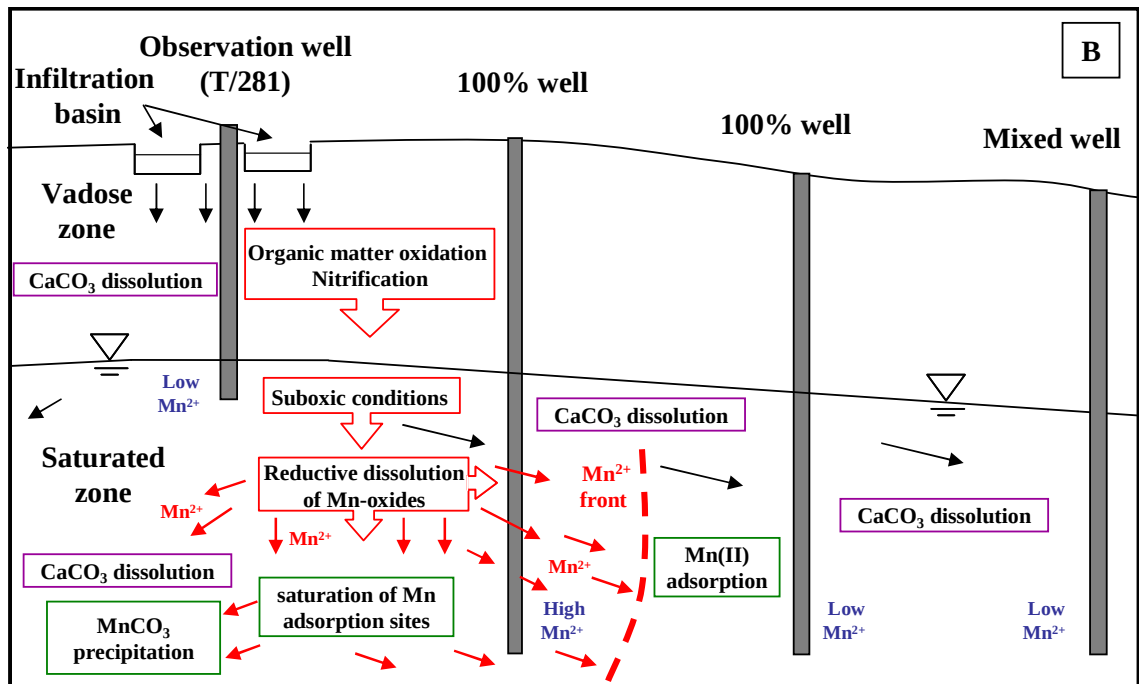


FIGURE 8.1: A three-stage (A,B,C) conceptual model describing the geochemical evolution and Mn mobilization along an aquifer recharged by effluents, e.g., the Yavne-2 SAT system of the Shafdan plant. The black arrows mark the water flow direction and the red arrows mark the dissolved Mn^{2+} transport. **A** - Suboxic conditions are established in the aquifer below the basin due to organic matter oxidation and nitrification in the vadose zone, causing reductive dissolution of Mn-oxides accompanied by immediate Mn(II) adsorption. Water-rock interactions including cation exchange and CaCO_3 dissolution alter the chemical composition of the effluents in the aquifer, until steady state is achieved. **B** - Mn adsorption sites become saturated and as a result the dissolved Mn^{2+} concentration increases and a high Mn^{2+} concentration front begins to advance in the direction of the groundwater flow in the aquifer area containing 100% effluents. Saturation with respect of MnCO_3 is attained. **C** - The high Mn^{2+} concentration front reaches the oxygenated mixing zone between the effluents and the fresh groundwater, where in addition to adsorption, the Mn^{2+} is oxidized and re-precipitates as Mn-oxides.



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List of Appendices

Appendix 1: Physical and chemical data of observation and production wells around the Yavne-2 basin from 2004 annual monitoring campaign.

Appendix 2: Physical and chemical data of observation and production wells around the Yavne-2 basin from 2005 annual monitoring campaign.

Appendix 3: Physical and chemical data of the new wells that were drilled during the present study.

Appendix 4: Chemical compositions of groundwater along the aquifer profiles in few representative wells, sampled by sealed sampler.

Appendix 5: Chemical compositions of the recharged effluents (RE) and the groundwater pumped from the 100% wells since the onset of the Yavne-2 basin operation, data from Mekorot Water Co..

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Appendix 8: Chemical and physical results of experiment 2 (EXP-2).

Appendix 9: Chemical and physical results of experiment 3 (EXP-3).

Appendix 10: Chemical and physical results of experiment 4 (EXP-4).

Appendix 11: Chemical and physical results of experiment 5 (EXP-5).

Appendix 12: Chemical and physical results of experiment 10 (EXP-10).

Appendix 13: Chemical and physical results of experiment 8 (EXP-8), to determine the cation exchange capacity (CEC) of the sediment and the cation distribution.

Appendix 14: Results of the leaching experiment at the end of experiment 5, to determine the cation exchange capacity (CEC) of the sediment and the cation distribution.

Appendix 15: 'MATLAB' codes of the numerical model.

המים. לפיכך, ספיחה של המנגן לסדימנטים של האקוויפר יוצרת חזית של ריכוזי מנגן גבוהים המתקדמת עם כיוון זרימת מי התהום. כאשר ריכוזי המנגן במי התהום גבוהים, שקיעה של $MnCO_3$ (רודוכרוזיט) מאיטה את עליית ריכוזו.

התקדמות החזית מוגבלת לאזור בו האקוויפר מכיל 100% קולחים. כאשר החזית תגיע לאזור הערבוב בין הקולחים לבין המים השפירים של האקוויפר הרגיונאלי, שהינם עשירי חמצן, המנגן יתחמצן וישקע כתחמוצות מנגן באקוויפר. לכן, בקידוחי ההפקה השואבים ערבוב של מי קולחים ומים שפירים, ריכוזי המנגן נמוכים ויש להניח שהם יישארו כך גם בעתיד. תהליך נידוד המנגן באקוויפר צפוי להסתיים כאשר כל תחמוצות המנגן הסדימנטריות הזמינות לחיזור בנפח האקוויפר המכיל 100% קולחים יחוזרו ויצרכו. מצב זה לא צפוי להתרחש בעשרות השנים הקרובות.

ושחרור של Ca^{2+} עד שהמערכת מגיעה לשיווי משקל בין הקולחים המוחדרים לסדימנטים של האקוויפר.

הקולחים המוחדרים לאקוויפר מכילים ריכוזים גבוהים יחסית של חומר אורגני מומס ושל אמוניום אשר מתחמצנים כמעט לחלוטין במהלך חלחול הקולחים בתווך הבלתי רווי. חמצון החומר האורגני והניטרפיקציה צורכים את החמצן המומס במים ויוצרים תנאים דלי חמצן המאפשרים חיזור של תחמוצות מנגן סדימנטריות וניוד של המנגן המחוזר עם מי התהום. יודגש כי המערכת אינה מגיעה לתנאים אנוקסיים (חסרי חמצן), ולכן לא מתקיימים בה חיזור ברזל או סולפאט.

מאזן המנגן, הבוחן את הכמות המצטברת של המנגן שנכנסה לאקוויפר עם הקולחים המוחדרים, לעומת הכמות שיצאה ממנו בקידוחי ההפקה בין השנים 1988-2004, מעיד על כך כי לפחות 8 טון של מנגן סדימנטרי מוצה (extracted) מסלעי האקוויפר בשנים אלו. עודף מנגן זה נובע בהכרח מניוד של מנגן סדימנטרי טבעי המצוי בסלעי האקוויפר.

ההופעה המאוחרת של ריכוזי המנגן הגבוהים בקידוחי ההפקה, והיווצרות חזית של ריכוזי מנגן גבוהים בתוך שטח האקוויפר המכיל 100% קולחים מצביעות על עיכוב של תנועת המנגן המומס המחוזר (Mn^{2+}) באקוויפר. עיכוב זה נגרם עקב ספיחה מיידי של המנגן המחוזר על הסדימנטים של האקוויפר, כפי שהתרחש גם בניסויי הסימולציה באמצעות קולונה במעבדה.

סימולציות המעבדה מוכיחות שעייכוב המנגן באקוויפר גדול במידה רבה לעומת עייכוב הקטיונים העיקריים. ואכן, המנגן התחיל להופיע בקולחים המושבים זמן רב לאחר שהקטיונים העיקריים הגיעו לשיווי משקל או למצב עמיד. התנהגות עקום הפריצה של המנגן המחוזר, Mn^{2+} , מוכתבת ע"י קיבולת הספיחה המקסימאלית של המנגן (Mn adsorption capacity). לכן, ככל שריכוז המנגן ב"תמיסת הכניסה" גבוה יותר, המנגן מופיע מוקדם יותר ב"תמיסת היציאה" ועליית עקום הפריצה חדה יותר. איזותרמת הספיחה של המנגן שהתקבלה מניסויי הקולונה מלמדת שכמות המנגן הכוללת שיכולה להיספח על גבי הסדימנטים באקוויפר במערכת ה-SAT של אגן יבנה-2 היא בטווח של 90-260 טון.

שקיעה של MnCO_3 (רודוכרוזיט) מגבילה את עליית ריכוזו של המנגן במי התהום כאשר ריכוזו גבוה (מעל $700 \mu\text{g}\cdot\text{L}^{-1}$ עבור $\text{pH}=6.8$, $\text{ALK}=0.005 \text{ eq}\cdot\text{L}^{-1}$). תוצאות המודל הנומרי, הכולל איברי הסעה וריאקציה כפי שזוהו באקוויפר, מראות שמקדם קצב שקיעת MnCO_3 נמוך ב-3 סדרי גודל לפחות ממקדם קצב הספיחה. מכך עולה שספיחה הינה התהליך העיקרי המכתיב את ניוד המנגן באקוויפר בתנאי דלי חמצן.

לסיכום, המודל הגיאוכימי הקונספטואלי שמסכם את תוצאות המחקר מציע שבאקוויפר חולי-קרבוונאטי הניזון ממים עשירים בחומר אורגני, תהליכי חמצון החומר האורגני וניטרפיקציה יוצרים תנאים דלי חמצן באקוויפר. בתנאים אלו חומר אורגני יכול להתחמצן ע"י תחמוצות מנגן סדימנטריות אשר מחוזרות למנגן מחוזר, Mn^{2+} , מסיס במים. המנגן המחוזר נספח באופן מיידי לסדימנטים של האקוויפר בהתאם למקדם החלוקה, K_d , של המנגן. רק כאשר כל אתרי הספיחה מגיעים לרוויה ביחס למנגן, ריכוזו במים עולה והתקדמותו באקוויפר מוכתבת ע"י הסעתו עם

תקציר

העבודה הנוכחית עוסקת בגיאוכימיה של מנגן (Mn) ובניודו באקוויפר חולי-קרבונאטי הניזון מהחדרת מים עשירים בחומר אורגני. המחקר נערך במערכת ה-SAT (Soil Aquifer Treatment) של מפעל השפד"ן, באתר החדרת הקולחים לקרקע ולאקוויפר המהווה את הטיפול השלישוני בקולחים. כפי שמתואר להלן, מערכת זו מהווה מודל מעולה למחקר גיאוכימי המשלב זיהוי וכימות של תהליכי ניוד מנגן במי תהום. מערכת ה-SAT כוללת החדרת קולחים שניוניים לאקוויפר החוף דרך חמישה אגני החדרה, והפקתם לאחר זמן שהייה של מספר חודשים באקוויפר באמצעות סדרה של קידוחי הפקה לשימוש חוזר בחקלאות. מאחר שהקולחים המוחדרים מכילים ריכוז גבוה של חומר אורגני מומס, תנאי החמצון-חיזור באקוויפר מאפשרים חיזור של תחמוצות מנגן וניוד של המנגן המחוזר עם מי התהום.

ריכוזי מנגן גבוהים ($100-2200 \mu\text{g}\cdot\text{L}^{-1}$) החלו להופיע במים המושבים לאחר כעשרים שנות החדרה, על אף שריכוזי המנגן במים המוחדרים היו ונשארו נמוכים ($30 \mu\text{g}\cdot\text{L}^{-1}$). עליה זו בריכוזי המנגן המומס לוותה בשקיעה מסיבית של תחמוצות מנגן בצנרת ההובלה של הקולחים המושבים (ה"קו השלישי"), אשר גרמה לסתימות במערכות ההשקיה הניזונות ממי השפד"ן. תצפיות אלו מצביעות על כך שהשפד"ן מהווה "מעבדה טבעית" טובה ללימוד הגיאוכימיה של המנגן וניודו במי תהום. בנוסף, להבנת הגיאוכימיה של המנגן בשפד"ן חשיבות יישומית רבה מכיוון שניוד המנגן ושקיעתו בצנרת יוצרים בעיה תפעולית חמורה של אספקת מים אמינה לצרכנים.

לאור האמור לעיל, מטרת המחקר היתה לזהות ולכמת את התהליכים הגיאוכימיים ואינטרקציות מים-סלע המשפיעים והמכתיבים את ניוד המנגן ואת הרכב מי התהום בתווך הבלתי רווי ובאקוויפר. דגש מיוחד הושם על התהליכים המכתיבים את עיכוב המנגן באקוויפר ואת העיכוב בהופעתו בקולחים המושבים. המחקר התמקד במערכת ה-SAT של אגן יבנה-2, בה נמדדו ריכוזי המנגן הגבוהים ביותר במי התהום.

שיטות העבודה כללו: 1. איסוף וניתוח הנתונים הגיאוכימיים ההיסטוריים של הקולחים המוחדרים ושל המים בקידוחים; 2. דיגום הקולחים המלחלים באגן ההחדרה ובחלק העליון (0-9 מ') של התווך הבלתי רווי, וכן דיגום של מי התהום בקידוחי התצפית וההפקה סביב האגן; 3. קדיחת חמישה קידוחי תצפית במרכז אגן ההחדרה ובמרחקים שונים ממנו, לצורך דיגום מים וסדימנטים; 4. אנליזות כימיות מפורטות לכל דוגמאות המים והסדימנטים; 5. ניסויי ספיחה וניוד מנגן במערכת מעבדתית באמצעות קולונה; 6. ניסוח מודל נומרי לתיאור עיכוב המנגן באקוויפר ו-7. ניתוח כמותי של הנתונים והצבת מודל גיאוכימי קונספטואלי המתאר את כלל התהליכים המתרחשים במערכת ה-SAT, בדגש על מערכת המנגן.

מניתוח ההרכב הכימי של מי התהום הנשאבים בקידוחי ההפקה ומניסויי הספיחה באמצעות קולונה עם סדימנטים מהשפד"ן עולה כי התהליכים העיקריים המשנים את ההרכב הכימי של הקולחים במהלך זרימתם באקוויפר הם חילוף קטיונים והמסה של CaCO_3 . בשלב הראשון של החדרת הקולחים לאקוויפר חל חילוף קטיונים משמעותי הכולל ספיחה של K^+ , Na^+ ו- Mg^{2+} .



משרד התשתיות הלאומיות
המכון הגיאולוגי

התפתחות גיאוכימית וניוד מנגן במים מועשרים בחומר אורגני המחלחלים לאקוויפר חולי-קרבונאטי; שיעור ממפעל השפד"ן לטיפול בשפכים

אורלי גורן

עבודת זו הוגשה כחיבור לקבלת תואר "דוקטור לפילוסופיה"
לסנאט האוניברסיטה העברית, ירושלים.

העבודה נעשתה בהדרכתם של:
ד"ר איתי גבריאלי, המכון הגיאולוגי, ירושלים
ד"ר אביהו בורג, המכון הגיאולוגי, ירושלים
פרופ' בעז לזר, המכון למדעי כדור הארץ, האוניברסיטה העברית, ירושלים