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# Chemical modifications of groundwater contaminated by recharge of treated sewage effluent

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## Abstract

Long-term monitoring of the chemical composition of recharge sewage effluent and associated contaminated groundwater from the Dan Region Sewage Reclamation Project shows, after 16 years of recharge operation, the presence of a distinct saline plume (up to 400 mg/l Cl), extending 1600 m downgradient in the Coastal Plain aquifer of Israel. The recorded electrolyte composition of groundwater in the vicinity of the recharge area reflects the variations in the compositions of the sewage effluents, as well as water–rock interactions induced by the recharge of treated sewage effluents. The original sewage composition was modified, particularly during early stages of effluent migration in the unsaturated zone, by cation-exchange and adsorption reactions. Since the soil sorption capacity is finite these reactions caused only limited modifications, and once the system reached a steady state the inorganic composition of the contaminated groundwater became similar to that of the recharge water. Decomposition of organic matter in the unsaturated zone resulted in CO<sub>2</sub> generation and dissolution of CaCO<sub>3</sub> minerals in the aquifer. It was shown that chemical and/or bio-degradation of organic matter takes place mainly in the unsaturated (vadose) zone. Hence, monitoring the efficiency of the vadose zone to retain contaminants is essential for evaluating the quality of groundwater since it was shown that organic compounds behave almost conservatively once the effluents enter and flow within the saturated zone.

## 1. Introduction

The quality of groundwater in Israel has been deteriorating rapidly during the last few decades. Identification of the sources of contamination and understanding pathways of contaminants to and within the aquifers are essential to the prediction of the quality of water as well as for an appropriate management of the water resources in Israel.

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Groundwater has been contaminated by anthropogenic sources such as intensive agriculture practices, irrigation with and seepage of treated, untreated or inadequately treated sewage, and industrial activity. About 70% of Israel's sewage water is either used as effluent for irrigation of agricultural crops or injected into the ground following a mechanical–biological treatment by activated sludge or oxidation ponds. These contamination processes are reflected by high nitrate concentrations (Kanfi et al., 1983; Ronen et al., 1983), high concentrations of labile organic matter (Ronen et al., 1987), the presence of heavy metals and synthetic, toxic organic materials (Magaritz et al., 1989, 1990; Wells et al., 1989), and the presence of nonbiodegradable (“hard”) nonionic detergents in both surface and groundwater (Zoller, 1992, and references therein).

It has been argued that the unsaturated (vadose) zone can filter and remove contaminants from effluent as it flows through it, thus functioning as a water purification system as well as a conduit to the underlying saturated zone (Andelman, 1994). The purpose of the present study is to evaluate the influence of the unsaturated zone on the electrolyte composition of groundwater contaminated by recharge of treated sewage effluent. The modifications of inorganic and organic constituents of sewage effluents during their flow from the recharge basins through the vadose zone to the saturated zone are investigated in treated sewage effluents from the Dan Region Sewage Reclamation Project and in associated contaminated groundwater from the underlying phreatic Coastal Plain aquifer of Israel (Fig. 1).

## 2. Hydrogeological background

The Coastal Plain aquifer in Israel is a phreatic aquifer, located along the Mediterranean sea coast. It varies in width from 7 km in the north to 20 km in the south; its thickness decreases eastwards from 200 m near the coastline to a few meters at the foothills of the Judea Mountains. The aquifer (the Kurkar Group of Pleistocene age) consists of interlayered sand, sandstone, calcareous sandstone (arenites), siltstone, red loamy soils, and marine clays of Pleistocene age, and it overlies the impervious marine clays of Pliocene age (the Saqiye Group). Intervening clay layers divide the western aquifer into 4–6 sub-aquifers up to 5–8 km inland from the coastline. In the central and eastern areas the aquifer is uniform and phreatic. The calcareous sandstone (arenites or “kurkar”) is composed of several minerals: quartz, feldspar, calcite, aragonite and iron oxides (Gavish and Friedman, 1969). A schematic cross-section from east to west in the study area (Fig. 2) exhibits an ~100-m-thick phreatic aquifer, with disconnected clay–silt layers at different depths. The high permeability of the sand and calcareous sandstone in the upper vadose zone enables rapid migration of sewage effluent to the saturated zone. The regional uncontaminated groundwater in that area is characterized by low salinity (< 30 mg/l Cl), Ca–HCO<sub>3</sub> type with a high Na/Cl ratio (Table 1).

## 3. The Dan region sewage reclamation project

The Dan Region Sewage Reclamation Project, located south of Tel Aviv (Fig. 1), collects, treats, and recharges municipal wastewater from the Dan metropolitan area (Tel

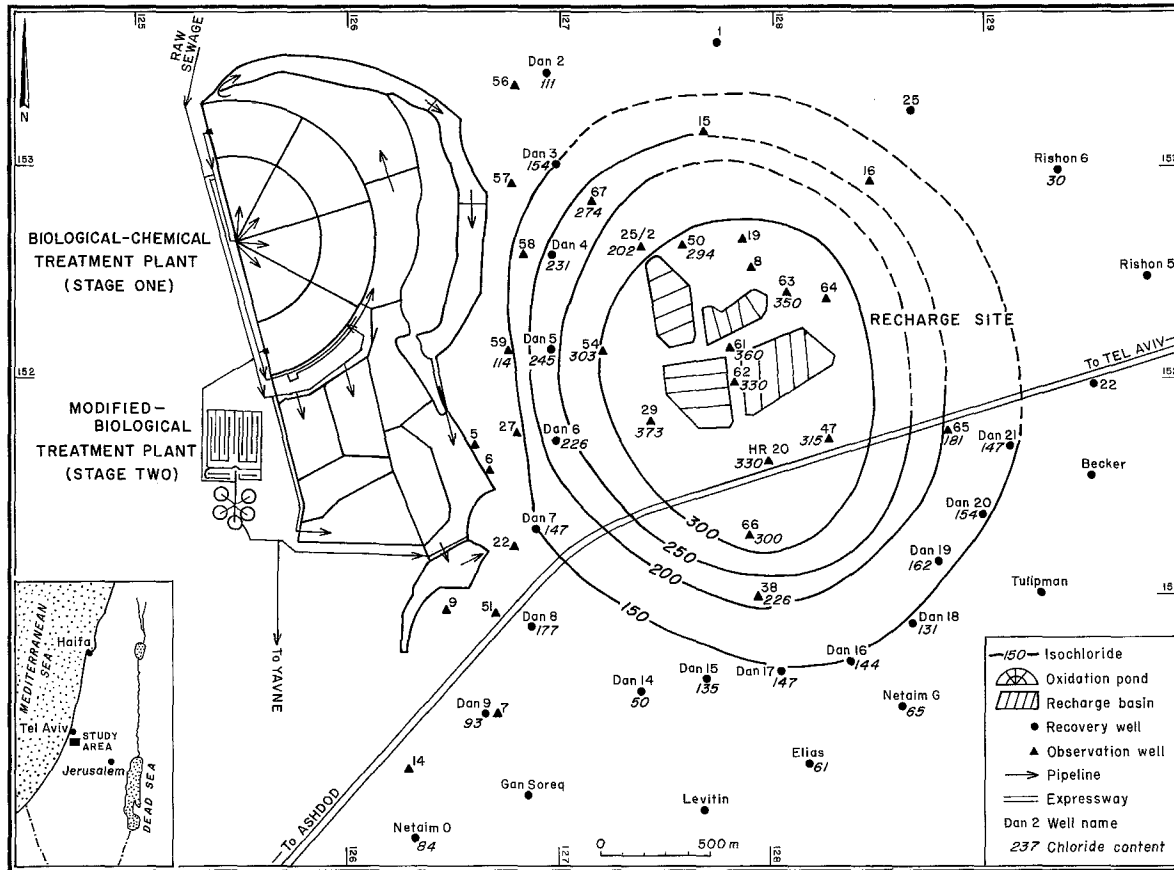


Fig. 1. Location maps of wells and spreading basins in the Dan region in Israel. Chloride contents of the investigated groundwater and iso-chloride lines (1992-1993), representing the spread of the treated sewage effluents in the aquifer, are included.

Table 1  
Chemical composition of selected groundwater samples from the Dan Region Sewage Reclamation Project

Source	Name	Date	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub>	B	DOC	Deter- gent	Na/Cl	Q*	Ca/Mg	K/Cl	SO <sub>4</sub> /Cl	B/Cl (× 10 <sup>-3</sup> )
Research well	T-61	1/7/77	43	5.6	12	0.6	17	13	138	2.7	0.013	–	0.01	1.09	0.85	4.66	0.032	0.28	2.51
Research well	T-61	11/12/77	132	8.5	22	0.7	207	41	98	0.8	0.037	2.00	0.04	0.16	2.69	9.42	0.003	0.07	0.587
Research well	T-61	2/6/86	72	6.3	142	2.0	172	22	305	0.7	0.390	3.60	0.41	1.27	0.66	6.94	0.011	0.05	7.44
Research well	T-61	23/3/93	155	12.9	241	30.8	364	98	420	35.0	0.353	–	–	1.02	0.87	7.31	0.077	0.10	3.18
Research well	T-61	7/6/93	168	13.9	241	31.0	355	110	448	47.0	0.600	4.00	0.05	1.05	0.87	7.32	0.079	0.11	5.55
Research well	T-66	23/3/93	148	18.0	232	1.0	300	105	478	15.0	0.340	–	–	1.19	0.74	4.98	0.003	0.13	3.72
Research well	T-66	7/6/93	145	18.4	200	1.0	272	88	452	15.0	0.304	2.70	0.13	1.13	0.78	4.77	0.003	0.12	3.67
Research well	T-66	5/2/91	134	17.7	156	2.0	289	96	333	0.6	0.340	4.00	0.20	0.83	0.90	4.59	0.006	0.12	3.86
Research well	T-20	23/3/93	133	11.8	236	18.5	330	83	407	4.0	0.412	–	–	1.10	0.79	6.83	0.051	0.09	4.10
Research well	T-20	7/6/93	160	11.1	232	16.7	346	103	426	5.0	0.756	5.00	0.13	1.03	0.88	8.74	0.044	0.11	7.17
Research well	T-54	7/6/93	136	12.0	223	17.8	303	80	433	11.0	0.491	3.70	0.14	1.13	0.78	6.89	0.053	0.10	5.32
Research well	T-54	23/3/93	139	13.2	232	18.5	303	90	454	14.0	0.569	–	–	1.18	0.75	6.40	0.055	0.11	6.16
Research well	T-38	23/3/93	82	15.8	141	4.3	226	75	176	14.0	0.131	–	–	0.96	0.92	3.14	0.017	0.12	1.90
Research well	T-38	7/6/93	109	16.6	147	4.4	225	75	258	25.0	0.148	1.90	0.05	1.01	0.94	3.99	0.018	0.12	2.16
Pumping well	Dan 6	7/6/93	112	13.8	147	4.1	211	60	294	28.0	0.226	–	–	1.07	0.92	4.94	0.018	0.10	3.52
Pumping well	Dan 6	23/3/93	116	14.0	155	4.7	229	68	304	26.0	0.275	–	–	1.04	0.91	5.04	0.019	0.11	3.94
Pumping well	Dan 17	23/3/93	97	11.6	65	1.0	149	34	206	14.0	0.065	–	–	0.67	1.19	5.09	0.006	0.08	1.43
Pumping well	Dan 17	7/6/93	96	11.6	63	1.0	140	34	208	15.0	0.133	–	–	0.70	1.16	5.00	0.006	0.09	3.12
Pumping well	Dan 5	7/6/93	121	13.0	173	4.0	245	75	317	29.0	0.281	–	–	1.09	0.89	5.64	0.015	0.11	3.67
Pumping well	Netayim C'	22/5/90	90	8.3	34	0.2	60	35	259	14.0	0.130	–	–	0.87	0.90	6.58	0.002	0.22	7.11
Pumping well	Netayim D'	28/5/90	64	9.2	26		40	21	198	5.2	0.160	–	–	1.00	0.87	4.22	0.000	0.19	13.1

Data from Kanarek et al. (1994). Results reported in mg/l, ratios in (mmol l<sup>-1</sup>)/(mmol l<sup>-1</sup>). Q\* = ratio in (meq l<sup>-1</sup>)/(meq l<sup>-1</sup>) of Ca/(HCO<sub>3</sub> + SO<sub>4</sub>).

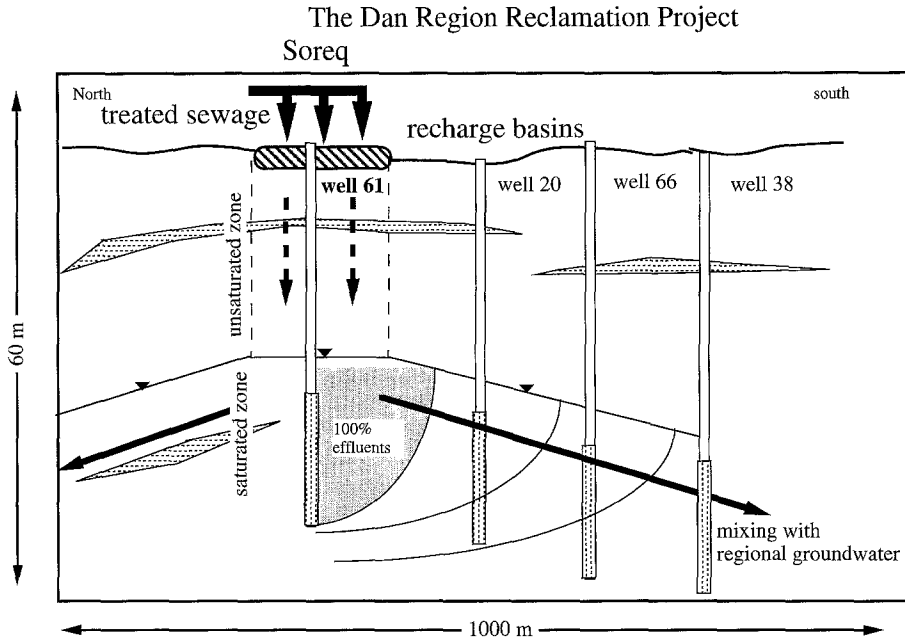


Fig. 2. A schematic hydrogeological cross-section from north to south in the study area.

Aviv–Jaffa and neighboring municipalities). The wastewater undergoes biological treatment in facultative oxidation ponds with recirculation, mechanical–biological treatment by activated sludge, and previously, chemical treatment by the high-lime–magnesium process followed by detention of the high-pH effluent in polishing ponds. Since 1989, however, the chemical treatment was discontinued and the process consists only of biological treatment. The effluent is recharged to the aquifer by means of spreading basins. The wastewater, mixed with regional groundwater, is collected by recovery wells located at a distance of  $\sim 2$  km from the recharge basins, and supplied for non-potable use (mainly irrigation) in the northwestern part of the Negev desert, Israel.

The present study reports the chemical composition of sewage effluent from the Dan Region as well as of groundwater collected from observation and recovery wells, located at different distances from the recharge basins (Table 1; Figs. 1 and 2), as recorded during the last 16 years (1977–1993) of the sewage plant operation. The present study is based on chemical data published in annual reports by Mekorot Water Company Ltd. (Kanarek et al., 1994 and references therein). The frequency of monitoring and analysis conducted by Mekorot Water Company varies from daily testing of sewage effluent samples to analysis of groundwater carried out every 2–6 months. Details of the analytical procedures are reported in Kanarek et al. (1994) and references therein.

Since the beginning of operation of the Dan Region Sewage Reclamation Project, during the period 1977–1993, a volume of  $\sim 252 \times 10^6$  m<sup>3</sup> of treated sewage effluent has been recharged to the aquifer (Kanarek et al., 1994 and references therein). The ion

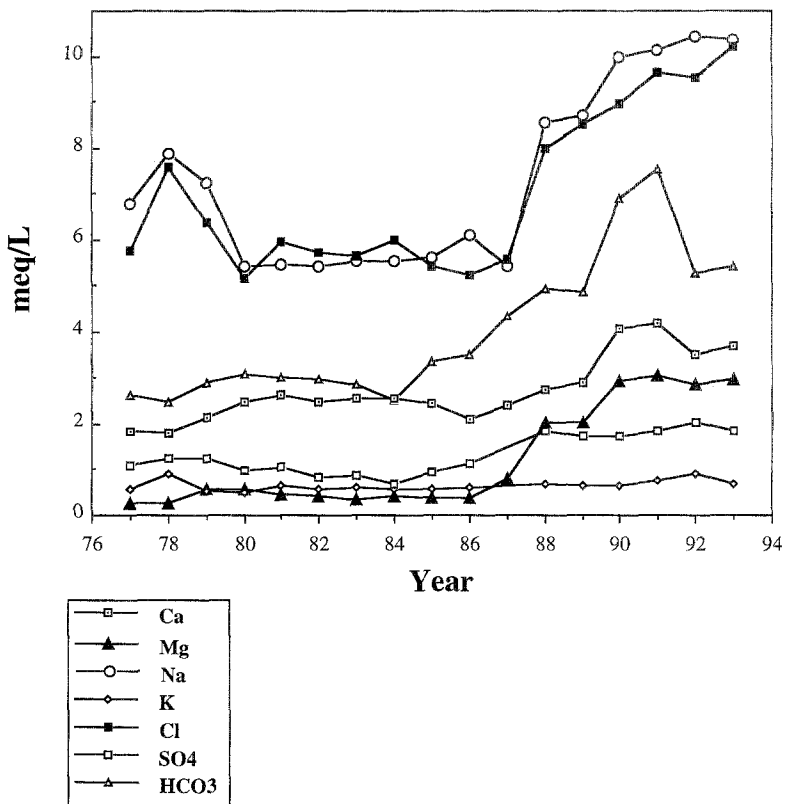


Fig. 3. Chemical variations of sewage effluents during the recharge period of 1977–1993.

variation of the treated sewage effluent over the years is summarized in Table 2 and Fig. 3.

The chloride concentrations (200–350 mg/l) in the effluent were higher than those of the regional uncontaminated groundwater in the Dan Region area (< 30 mg/l; Table 1). Hofman (1993) has shown that the anthropogenic sources of chloride and sodium in waste waters in Israel derive mainly from extensive industrial and domestic applications of NaCl salts as well as the use of Na in domestic and industrial cleaning products. The net inputs of anthropogenic chloride and sodium are estimated as 125 and 119 mg/l, respectively (Hofman, 1993). The relatively high boron concentrations (0.3–0.6 mg/l) in the sewage effluent reflect the use of boron compounds, in particular sodium perborate as an oxidation bleaching agent in domestic and industrial cleaning products (Vengosh et al., 1994). During 1987, a sharp increase of chloride, sodium, magnesium, and boron concentrations in the effluent was observed. The increase was due to additional wastewater that was supplied from municipalities and industrial areas to the Dan Region Sewage Reclamation Project.

Overall, the inorganic composition of the treated sewage is almost identical to that of

Table 2  
The annual average composition of treated sewage effluent that was recharged to the aquifer

Year	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub>	B	TDS	P	BOD	COD	DOC	Detrg	Na/Cl	Q*	Ca/Mg	K/Cl	SO <sub>4</sub> /Cl	B/Cl (× 10 <sup>-3</sup> )
1977	37	3.3	156	22	204	52	161	0.40	0.48	636	1.5	3.0	57	20	1.8	1.18	0.50	6.80	0.098	0.09	7.72
1978	36	3.1	181	36	268	60	151	0.62	0.30	736	0.8	3.5	46	12	1.2	1.04	0.48	7.05	0.122	0.08	3.67
1979	43	6.9	166	21	226	59	177	0.58	0.30	700	1.3	4.9	39	11	1.1	1.13	0.52	3.78	0.084	0.10	4.36
1980	50	7.0	125	19	183	47	189	0.71	0.34	621	2.2	4.5	41	21	0.9	1.05	0.61	4.33	0.094	0.09	6.10
1981	53	5.6	126	25	211	50	184	0.58	0.36	656	3.2	5.7	46	20	3.2	0.92	0.65	5.74	0.107	0.09	5.60
1982	50	5.2	125	22	203	40	182	0.31	0.27	628	2.2	5.9	52	21	1.3	0.95	0.65	5.84	0.098	0.07	4.37
1983	51	4.1	127	23	200	41	174	0.97	0.27	622	2.0	5.3	37	15	1.4	0.98	0.69	7.55	0.104	0.08	4.43
1984	51	5.0	127	22	212	33	155	0.71	0.25	606	1.6	4.1	37	17	1.1	0.92	0.79	6.19	0.094	0.06	3.87
1985	49	4.4	129	22	192	45	205	0.97	0.26	648	2.9	4.4	48	16	1.4	1.04	0.57	6.76	0.104	0.09	4.44
1986	42	4.8	140	24	186	54	215	0.44	0.40	666	3.2	6.4	57	26	1.9	1.16	0.45	5.31	0.117	0.11	7.06
1987	48	9.7	125		198		265	0.13	0.30	646	3.3	6.3	52	24	3.2	0.97	0.55	3.00	0.000	0.00	4.97
1988	55	24.9	197	27	283	88	300	0.23	0.40	976	2.8	5.8	50	21	0.6	1.07	0.41	1.34	0.087	0.11	4.64
1989	58	24.9	200	25	302	84	296	0.27	0.40	991	3.0	5.0	49	19	0.6	1.02	0.44	1.41	0.075	0.10	4.35
1990	81	35.8	230	25	318	84	420	3.72	0.50	1198	5.3	5.8	68	18	0.5	1.12	0.47	1.37	0.071	0.10	5.16
1991	84	37.0	233	29	342	88	460		0.50	1273	5.9	9.2	69	18	0.5	1.05	0.45	1.38	0.077	0.09	4.80
1992	70	34.7	240	35	338	98	322	0.05	0.54	1139	4.0	6.0	70	16	0.5	1.10	0.48	1.23	0.094	0.11	5.24
1993	74	36.0	238	26	362	88	330	0.06	0.54	1155	6.1	5.9	71	17	0.4	1.01	0.51	1.25	0.065	0.09	4.90

Data from Kanarek et al. (1994) and references therein. Chemical data in mg/l; ratios are in (mol l<sup>-1</sup>)/(mol l<sup>-1</sup>). Q\* = ratio in (meq l<sup>-1</sup>)/(meq l<sup>-1</sup>) of Ca/(HCO<sub>3</sub> + SO<sub>4</sub>).

the raw waste water, thus indicating that it is not affected by mechanical–biological treatment by activated sludge or facultative oxidation ponds.

#### 4. Composition modifications of inorganic constituents

The electrolyte compositions of groundwater sampled from well 61, located between the recharge basins (Fig. 1), are used to monitor the interactions of the sewage effluent in the unsaturated zone. The “breakthrough” curve of chloride, which is assumed to behave conservatively in the aquifer, reflects the arrival of the effluent through the 30 m of the unsaturated zone. The chloride variations suggest an arrival time of 6 months from the ground surface to the saturated zone. Therefore the concentration of the major inorganic ions in groundwater sampled from well 61 ( $C_i$ ) were compared to those of the annual average of the recharge effluents from the same year ( $C_o$ ). This comparison is justified because of the rapid (6 months) penetration of the effluents through the unsaturated zone. The variations of  $C_i/C_o$  over time are presented in Fig. 4. It should be noted that the normalization of  $C_i/C_o$  is valid for the period of 1977–1987, when the ion concentrations of the effluents were constant (Fig. 3). The data show that while the concentrations of Cl, Na,  $SO_4$ , and B approached those in the co-existing effluents (i.e.  $C_i/C_o$  ratio reached 1), the concentrations of Ca, Mg, K, and  $HCO_3$  were modified relative to those in the recharged effluent during most of the recharge period.

While the arrival time of chloride through the unsaturated zone took 0.5 yr, the arrival time of sodium and boron was almost 2 yr (i.e. the  $C_i/C_o$  ratios of Na and B reached unity only at the beginning of 1979; Fig. 4). The delay of  $\sim 2$  yr in the arrival of Na and B relative to that of chloride is explained by their interaction with the aquifer rocks, in particular with clay minerals. During the delay period of 1978–1979, the  $C_i/C_o$  ratios for Ca were conspicuously high (Fig. 4) with Ca concentration of 6.6 meq/l in the contaminated groundwater. Moreover, the variations of Na/Cl and Ca/( $HCO_3 + SO_4$ ) ratios over time (Fig. 5) show that low Na/Cl ratios (as low as 0.1) during the delay period of 1978–1979 correspond to a Ca enrichment with Ca/( $HCO_3 + SO_4$ ) ratio  $> 1$ . These relationships suggest that cation-exchange reactions might control the ion composition of the contaminated groundwater. The effect of the cation-exchange reactions is limited, however, to relatively short periods and to the exchangeable sodium percentage (ESP) of clay minerals in the aquifer. It seems that cation-exchange reactions occur mainly during the first stages of effluent arrival to the aquifer. Once the exchangeable sites become saturated, Na is not retained from the effluents and behaves conservatively like the chloride ion.

Similarly, the delay in the arrival of boron is attributed to the adsorption of boron onto clay minerals in the unsaturated zone. After 2 yr of continuous recharge of effluents enriched in boron, the adsorption sites became saturated with respect to boron. Consequently, boron was not removed to the solid phase and the boron concentrations in the contaminated groundwater became identical to those in the sewage effluents. Vengosh et al. (1994) have shown that the boron isotope composition of contaminated groundwater in the vicinity of the Dan Region reflects both the recharge of sewage effluent with a distinctive isotopic composition and boron adsorption onto clay minerals.



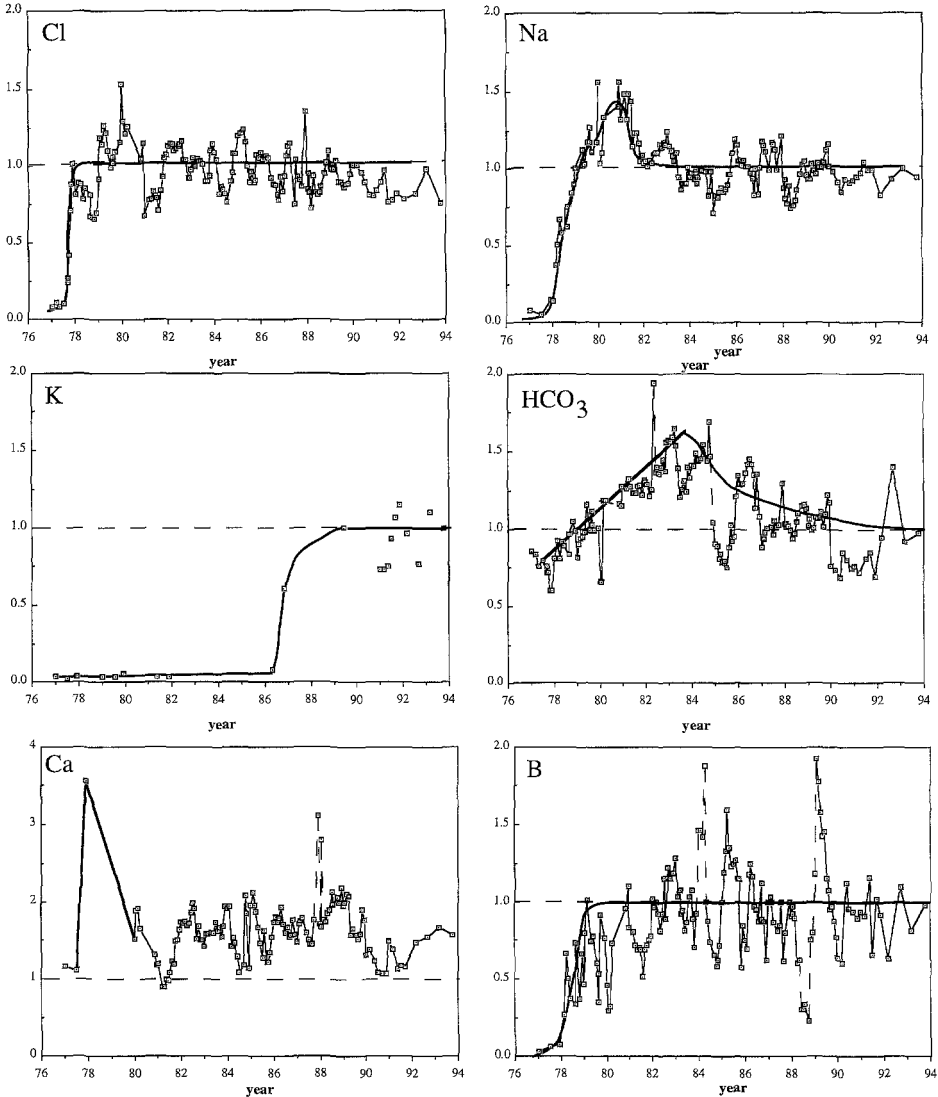


Fig. 4. Variations of  $C_i/C_o$  ratios (the ratio between the concentrations in contaminated groundwater from well 61 to that in recharged sewage effluent) through time of different ions. Note the delay of the arrival times (i.e. "breakthrough" defined as  $C_i/C_o = 1$ ) of Na, K, and B, and the high concentrations of Ca during early stages of effluent recharge.

The potassium concentration of the contaminated groundwater during the period 1977–1987 was significantly lower than that of the effluent. This suggests adsorption of K onto clay minerals in the unsaturated zone. The increase of K concentrations from 1987, which reached  $C_i/C_o = 1$  during 1989 (Fig. 4), suggests that the adsorption sites

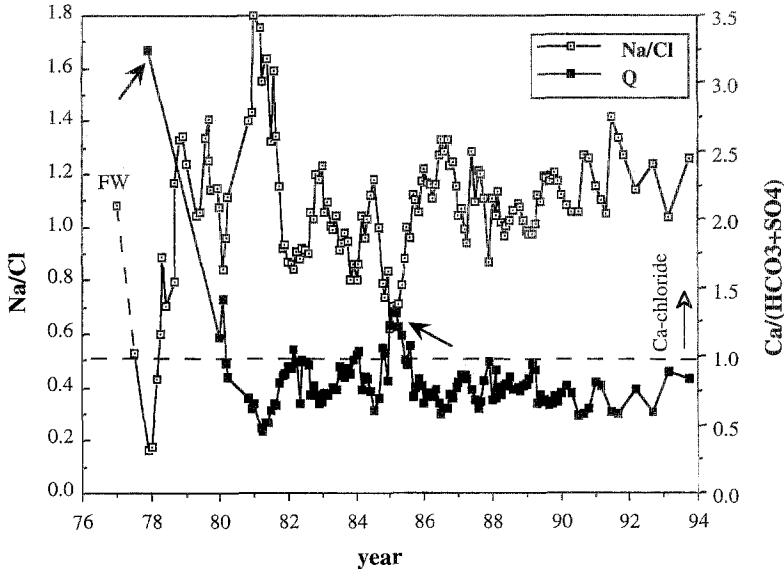


Fig. 5. Variations of Na/Cl and Ca/(HCO<sub>3</sub> + SO<sub>4</sub>) ratios through time in contaminated groundwater from well 61. Note the low Na/Cl ratios that correspond to high Ca/(HCO<sub>3</sub> + SO<sub>4</sub>) ratios during early stages of effluent recharge. These modifications are attributed to cation-exchange reactions which modified the contaminated groundwater into CaCl<sub>2</sub> water [i.e. Ca/(HCO<sub>3</sub> + SO<sub>4</sub>) > 1]. During most of the recharge period the Na/Cl and Ca/(HCO<sub>3</sub> + SO<sub>4</sub>) variations were identical to those in the sewage effluent.

of the clay minerals reached a steady state with respect to potassium. It is well known that the efficiency of clay minerals such as montmorillonite to K is much greater than that for Na. Consequently, the potassium content of the groundwater became similar to that of the effluent only during the last 5 years.

The average content of adsorbed K can be estimated by assuming that the recharge basins area is  $320 \times 10^3$  m<sup>2</sup>, the depth of the unsaturated zone is 30 m, the rock density is  $1.5 \times 10^{-3}$  kg/m<sup>3</sup> (which equals a rock mass of  $1.4 \times 10^{10}$  kg), clay minerals content of  $\sim 10\%$  of the aquifer rocks [resulting in a rock mass of  $1.4 \times 10^9$  kg ( $M_{\text{clay}}$ )], the effluent volume is  $131 \times 10^6$  m<sup>3</sup> with potassium concentrations of 24 mg/l that was recharged to the aquifer during 1977–1987, and that the average K concentration of the contaminated groundwater during that period was only 1 mg/l. Thus, under these assumptions an amount of  $3 \times 10^6$  kg K [i.e.  $Q_k = \text{effluent volume} \times \text{concentration} (K_{\text{effluent}} - K_{\text{groundwater}})$ ] was adsorbed or fixed by the clay surface (= 0.05 meq/g clay).

The calcium concentration in the contaminated groundwater was higher than that in the sewage effluent, by 2–4 meq/l between the years 1977–1987 (see Fig. 4). A similar, but not identical, enrichment of HCO<sub>3</sub> suggests that this is due to carbonate dissolution. It is possible that dissolution of calcite was enhanced by the pressure of higher CO<sub>2</sub> partial pressure in the vadose zone due to the degradation of organic matter which is present in the recharged effluent.

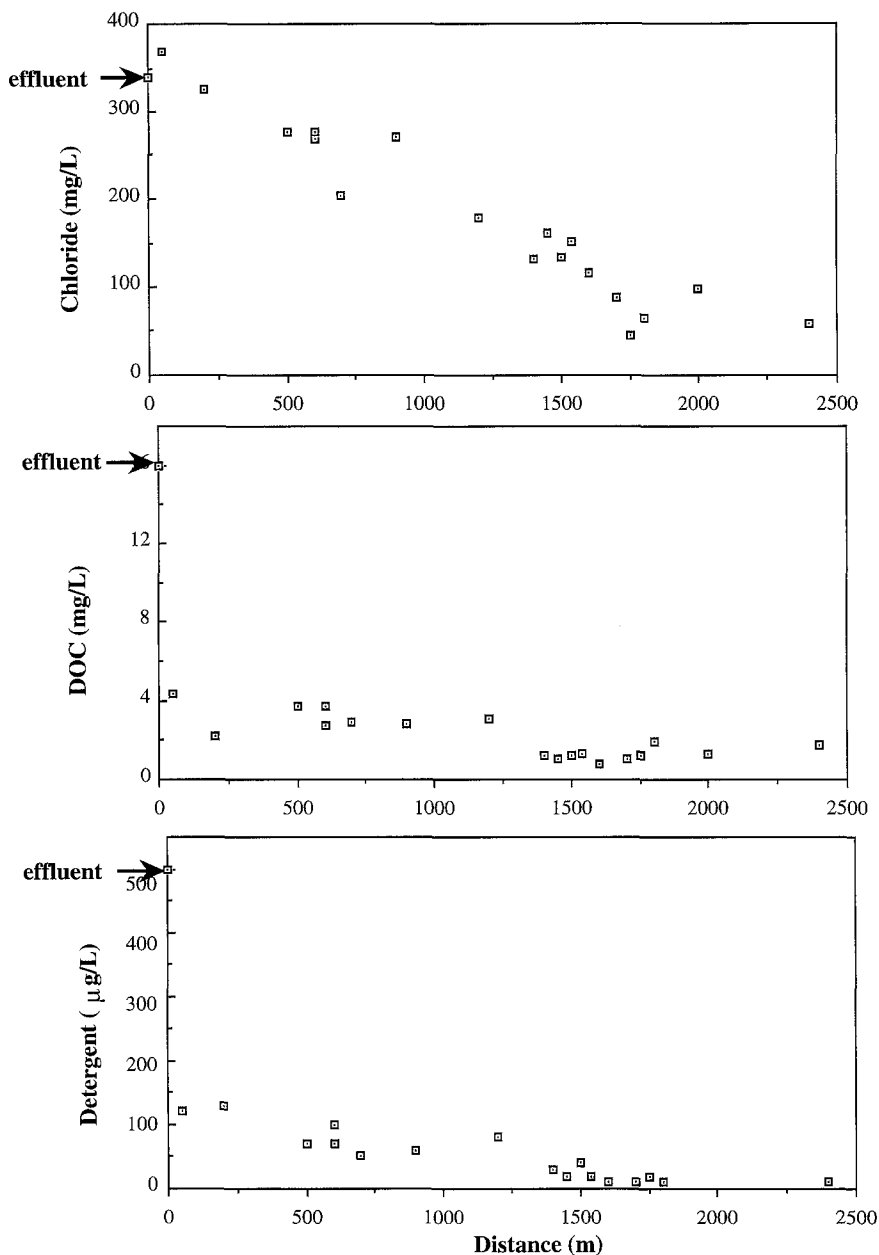


Fig. 6. Concentrations of chloride, DOC, and detergents versus distances of wells from the recharge basins. Arrows represent values of the sewage effluents. The gradual decrease of chloride concentrations reflects mixing with uncontaminated regional groundwater, whereas the abrupt reduction in the concentration of organic matter reflects biodegradation of organic matter in the vadose zone.

## 5. Degradation of organic matter

The chloride concentration of contaminated groundwater in the vicinity of the Dan Region plant was used to monitor the degree of mixing of the sewage effluent with regional groundwater and hence their degree of contamination (Kanarek et al., 1994 and references therein). A gradual decrease in chloride content with distance from the

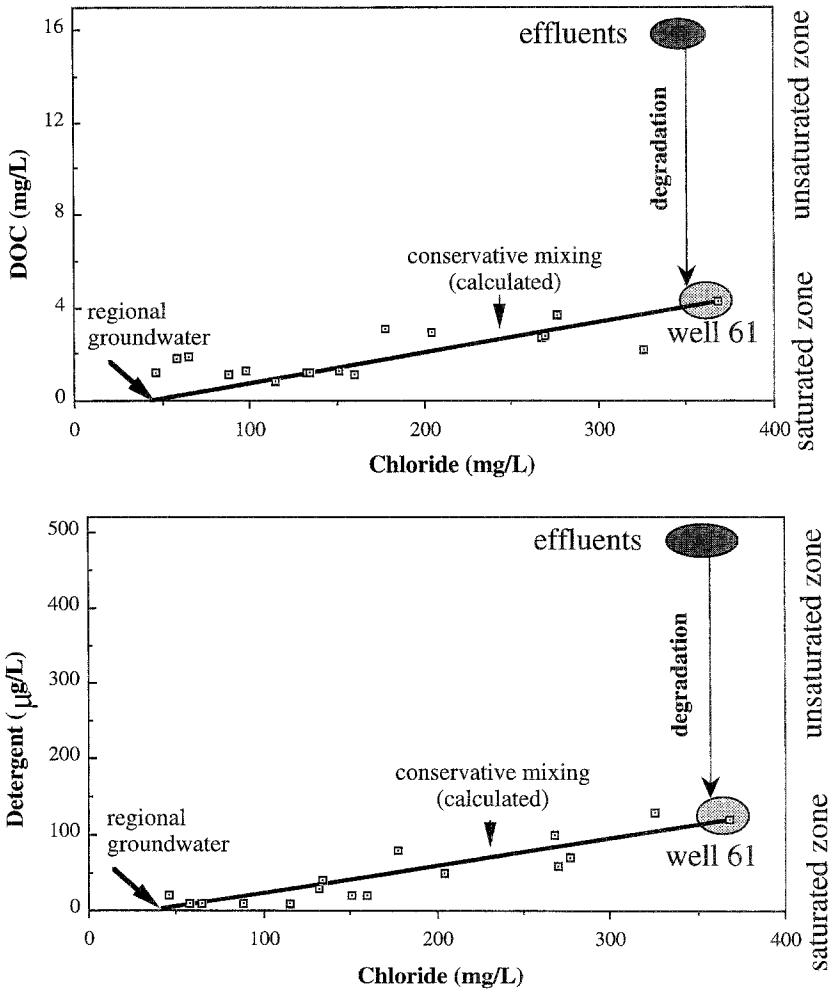


Fig. 7. Chloride versus DOC and detergent concentrations in groundwater representing the unsaturated zone (well 61) and the saturated zone at different distances from the recharge basins. The data points are compared to the theoretical mixing curves between contaminated groundwater from the unsaturated zone (e.g., well 61) and regional uncontaminated groundwaters (DOC = 0; Cl  $\approx$  50 mg/l). The consistency of the data points with the theoretical mixing lines suggests that organic matter behaves conservatively (i.e. no degradation) during the flow of effluent within the saturated zone.

recharge basins (Fig. 6) reflects the flow of effluents in the aquifer and dilution with the regional groundwater.

In contrast to chloride, the concentrations of organic matter, represented by DOC and detergents, show a significant depletion in wells located under the recharge basins (e.g., well 61) and only a slight gradual decrease with distance within the saturated zone (Fig. 6). The concentrations of DOC and detergents in contaminated groundwater from well 61, sampled during 1993, were compared to those in sewage effluent of that year. The significant depletion of the organic constituents emphasizes the role of the unsaturated (vadose) zone as a purification system for organic contaminants. The removal mechanisms can be volatilization and escape to the atmosphere, biodegradation and chemical or biological transformation to new forms, as well as adsorption to soil mineral surface or organic particles (Andelman, 1994).

Most soil–aquifer treatment processes take place in the upper part of the vadose zone due to greater organic matter content, unsaturated flow, and supply of oxygen in the aerobic area (Andelman, 1994). This is clearly demonstrated in this study. The gradual decrease of DOC and detergent concentrations in the contaminated groundwater within the saturated zone corresponds to calculated mixing curves between contaminated groundwater in the unsaturated zone (i.e. well 61) and regional uncontaminated groundwater (Fig. 7). Thus the concentrations of organic constituents in the saturated zone are controlled mainly by mixing processes. This implies that the degradation of organic matter takes place mainly in the unsaturated zone and only a small fraction, if any, of organic matter is removed in the saturated zone. This demonstrates the importance of the unsaturated zone in controlling the quality of groundwater by early degradation of organic matters.

## 6. Conclusions

Dissolved inorganic salts are not altered, nor are they retained in most conventional wastewater treatment processes. Reconstruction of the modifications of inorganic constituents of treated sewage effluents from the Dan Region Sewage Reclamation Project during their flow through the vadose zone of the Coastal Plain aquifer of Israel showed that groundwater from the phreatic aquifer responds to recharge of sewage effluent by an increase in the salinity and changes in its chemical composition. The recharge of effluent with relatively high salinity (a range of 200–380 mgCl/l) and a Na–Cl composition into fresh groundwater (< 30 mgCl/l) with a Ca–HCO<sub>3</sub> composition resulted in cation-exchange and adsorption reactions, particularly during the early phases of recharge effluent. The effect of the cation-exchange and adsorption reactions is limited, however, to relatively short periods and to the exchangeable sodium percentage (ESP) of clay minerals in the aquifer. Once the exchangeable and adsorbed sites become saturated, Na, K, and B are retained in the effluents and behave conservatively in the vadose zone. It seems that the limited capacity of clay minerals can control the ability of the unsaturated zone to retain also other contaminants such as heavy metals or organic matter. Consequently, long-term recharge of sewage effluents with high levels of these elements will be reflected in the composition of contaminated groundwater in underlying

phreatic aquifers. Monitoring of elements that are sensitive to clay–water interactions (e.g., Na, K, B) can be used to predict and as alarm signals for reduction in the function of the vadose zone as a water purification system.

We have shown that degradation of organic matter takes place mainly in the vadose zone and only a small fraction of organic matter is removed during the flow of contaminated groundwater in the saturated zone. The vadose zone controls the quality of groundwater in a phreatic aquifer by early degradation of organic matters, thus monitoring the efficiency of the purification processes in the vadose zone is essential for evaluating the quality of groundwater contaminated by artificial recharge of treated wastewater of impaired quality.

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### References

- Andelman, J., 1994. Ground Water Recharge Using Waters of Impaired Quality. Comm. Ground Water Recharge, Water Sci. Technol. Board, Natl. Res. Council, Natl. Academy Press, Washington, DC, 283 pp.
- Gavish, E. and Friedman, G.M., 1969. Progressive diagenesis in Quaternary to Late Tertiary carbonate sediments: sequence and time scale. *J. Sediment. Petrol.*, 39: 980–1006.
- Hofman, D., 1993. Application of nanofiltration and potassium for reducing salinity in municipal effluents. Water Comm., Jerusalem, Rep. (in Hebrew).
- Kanarek, A., Aharoni, A., Michail, M., Kogan, I. and Sheree, D., 1994. Groundwater recharge with municipal effluent: Recharge basins Soreq, Yavne 1 and Yavne 2. Dan Region Reclam. Proj., Mekorot Water Co. Ltd., Cent. District, Dan Region Unit. Annu. Rep., 261 pp.
- Kanfi, Y., Ronen, D. and Magaritz, M., 1983. Nitrate trends in the Coastal Plain aquifer of Israel. *J. Hydrol.*, 66: 331–341.
- Magaritz, M., Wells, M.C., Amiel, A. and Ronen, D., 1989. Application of multi-layer sampler based on the dialysis cell technique for the study of trace metals in groundwater. *Appl. Geochem.*, 4: 617–624.
- Magaritz, M., Amiel, A., Ronen, D. and Wells, M.C., 1990. Distribution of metals in a polluted aquifer: A comparison of aquifer suspended material to fine sediments of the adjacent environment. *J. Contam. Hydrol.*, 5: 333–347.
- Ronen, D., Kanfi, Y. and Magaritz, M., 1983. Sources of nitrates in groundwater of the Coastal Plain of Israel (evolution of ideas). *Water Resour. Res.*, 17: 1499–1503.
- Ronen, D., Magaritz, M., Almon, E. and Amiel, A., 1987. Anthropogenic anoxification (‘‘eutrophication’’) of the water table region of a deep phreatic aquifer. *Water Resour. Res.*, 23: 1554–1560.
- Vengosh, A., Heumann, K.G., Juraske, S. and Kasher R., 1994. Boron isotope application for tracing sources of contamination in groundwater. *Environ. Sci. Technol.*, 28: 1968–1974.
- Wells, M.C., Magaritz, M., Amiel, A., Rophe, B. and Ronen, D., 1989. Determination of in situ metal partitioning between particulate matter and groundwater. *Naturwissenschaften*, 76: 568–570.
- Zoller, U., 1992. Distribution and survival of nonionic surfactants in the surface, sea and groundwater of Israel. *J. Environ. Sci. Health*, A27(6): 1521–1533.