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The impact of freshwater and wastewater irrigation on the chemistry of shallow groundwater: a case study from the Israeli Coastal Aquifer

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Abstract

Differences in the impact of irrigation with freshwater versus wastewater on the underlying shallow groundwater quality were investigated in the Coastal Aquifer of Israel. Seven research boreholes were drilled to the top-most 3–5 m of the saturated zone (the water table region-WTR) in the agricultural fields. The unsaturated zone and the WTR below the irrigated fields consist mainly of clayey sands, while the main aquifer comprises mainly of calcareous sandstones and sands. We show that the salinity and composition of the groundwater at the WTR are highly variable over a distance of less than 1 km and are controlled by the irrigating water and the processes in the overlying unsaturated zone. Tritium data in this groundwater (4.6 tritium units (TU)) support that these water are modern recharge. The water at the WTR is more saline and has a different chemical composition relative to the overlying irrigation water. High SAR values (sodium adsorption ratio) in wastewater irrigation lead to absorption of Na^+ onto the clay and release of Ca^{2+} into the recharging water, resulting in low Na/Cl (0.4 compared to 1.2 in the wastewater) and high Ca/Cl ratios. In contrast, in the freshwater-irrigated field the irrigation water pumped from the aquifer (Na/Cl = 0.9; SAR = 0.6) is modified into Na-rich groundwater (Na/Cl = 2.0) due to reverse base-exchange reactions. The high NO_3 concentration (>100 mg/l) in the WTR below both fields is derived from the agricultural activities. In the freshwater field, the source of NO_3 is fertilizer leachates, whereas in the wastewater field, where less fertilizers are applied, nitrate is probably derived from nitrification of the NH_4 in the wastewater. Some of the original inorganic nitrogen in the wastewater is consumed by the agricultural plants, resulting in a lower inorganic-N/Cl ratio in the WTR as compared to that in the wastewater. This study demonstrates the important role of the composition of irrigation water, combined with lithology and land use, in determining the quality of the water that recharge the aquifer below agricultural fields.

Keywords: Groundwater salinization; Groundwater contamination; Irrigation; Wastewater; Base exchange; Coastal Aquifer; Water table region; Unsaturated zone

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1. Introduction

One of the most severe problems concerning groundwater quality is rapid salinization of water resources. The increase in groundwater salinity, particularly in coastal areas, may be due to influx of natural saline water, such as sea water intrusion, dissolution of soluble salts in the unsaturated zone, upconing and the flow of natural-derived saline water from adjacent aquifers (e.g. Vengosh and Rosenthal, 1994; Vengosh et al., 1999; Maslia and Prowell, 1990; Jones et al., 1999, Allison et al., 1990; Banner et al., 1989; Herczeg et al., 1991; Rosenthal et al., 1992). Anthropogenic contamination is another major cause of salinization and water-quality degradation. One of its most pronounced impacts is increase in the nitrate concentration which is derived from infiltration of sewage effluents, industrial wastes and agriculture return flows (Hern and Feltz, 1998; Hao and Change, 2002; Glen et al., 1999; Mitchel et al., 2000; DeSimone et al., 1997; Vengosh and Keren, 1996). Part of the nitrate contamination is from natural nitrogen (N) in the soil, released to the unsaturated zone due to intense cultivation of virgin soil. Other sources of N can be derived from fertilizers, wastewater irrigation and breakdown of remnants of the growing crops (Kanfi et al., 1983; Ronen et al., 1983).

In phreatic aquifers, irrigation by groundwater causes recycling of salts and their accumulation in the aquifer. The salts are accumulated in the soil and flushed through the unsaturated zone to the aquifer. Moreover, irrigation with wastewater, which is generally more saline than regional groundwater, increases the rate of salinization of shallow groundwater. This problem is more conspicuous in arid and semi-arid zones where potable water is replaced by wastewater for irrigation in order to save the depleting water resources.

Groundwater salinization and degradation is usually observed through sampling of pumping wells. In these wells, the screens are located in the deeper parts of the aquifer, far below the water table. However, the salt load originating from anthropogenic sources such as agricultural activity can be best evaluated at the water table region (WTR) where it first arrives. Nevertheless, only a few studies have investigated this region (e.g. Ronen and Magaritz, 1985). Here, we demonstrate that the water quality of shallow groundwater in a phreatic aquifer is impacted by long-term (>20 years) irrigation. We show that the factors controlling the salinity and composition of groundwater at the WTR are the chemical composition of the irrigation water and the water-rock interaction in the unsaturated zone. Over the long-run, the water at the WTR mixes with the regional aquifer, and the additional salt load derived from irrigation, leads to groundwater salinization.

1.1. Geohydrological background

The Coastal Aquifer underlies the Coastal Plain of Israel and runs parallel to the Mediterranean Sea, extending east between 8 km in the north to about 30 km in the south (Fig. 1). The Kurkar Group which forms the aquifer, overlies the impervious marine clays of the Saqiye Group of Neogene age and is composed of alternations of sandstone, calcareous sandstone (eolianites or ‘Kurkar’), siltstone, red sandstones and loamy soils (‘Hamra‘), and marine clay and shales of Pleistocene age (Issar, 1968; Nativ and Weisbrod, 1994; Fig. 2). The latter divide the aquifer into a number of sub-units but the aquifer is generally considered as a single water system. The main recharge to the aquifer is from rain that falls directly above it (average rainfall of 500 mm/yr in the central area and less than 300 mm/yr in the south). The general flow direction in the aquifer is from the east towards the Mediterranean Sea in the west. Morphologically, the Coastal Plain is characterized by a series of parallel north-south ridges, made of calcareous sandstone or partly cemented sand dunes that run parallel to the shore line with clayey longitudinal valleys (‘trough’) between them (Issar, 1968; Tolmach, 1977). These troughs were once swamps or riverbeds and their soil is therefore fertile. Much of the agriculture cultivation over the Coastal Plain is done in these troughs, which are widely irrigated with wastewater. Generally, the western-most part of the Coastal Plain comprises mostly of dunes with little soils or clays.

1.2. Salinization of the coastal plain

The chlorinity of groundwater in the aquifer during the 1930 s generally did not exceed 100 mg/Cl.

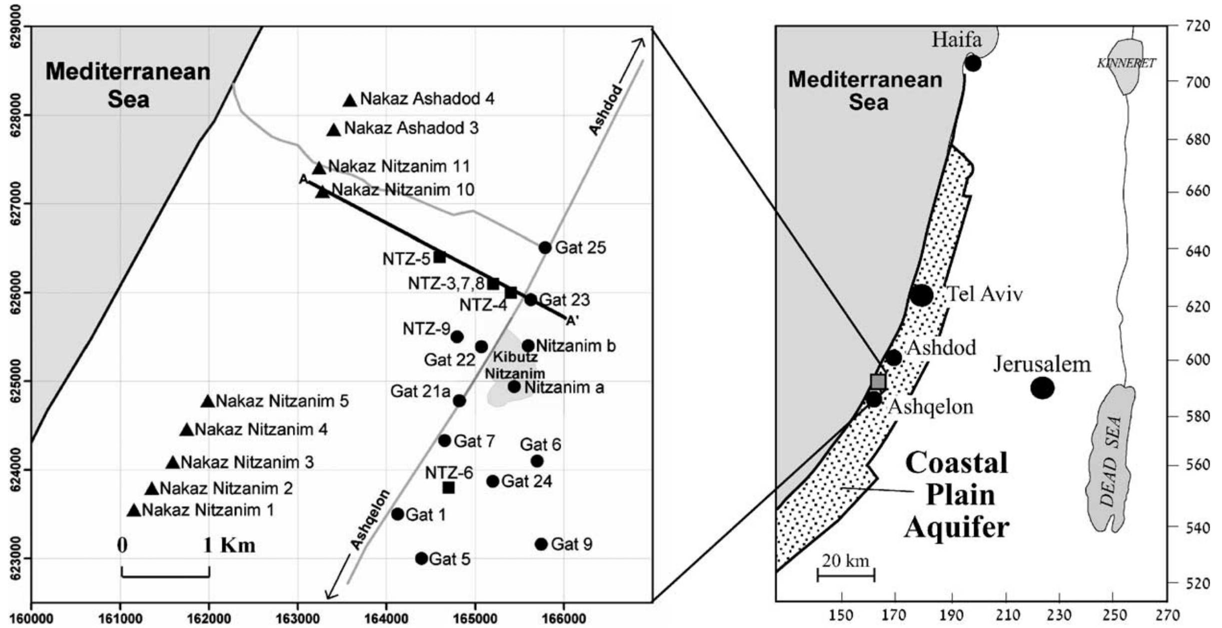

Fig. 1. Location map, including pumping and new research wells (Israel grid). Triangles: Nakaz wells; circles: Gat wells; squares: new research wells. Line A–A′ is the location of the geological cross section presented in Fig. 4.

The high quality of groundwater in the aquifer has since been impaired due to salinization processes along the western and eastern margins, as well as in internal areas of the aquifer in the form of salt plumes (Mercado et al., 1977; Mercado, 1985; Vengosh and Rosenthal, 1994; Vengosh et al., 1999). The degradation in the water quality of the aquifer is manifested in an increase in the average concentrations of chloride and nitrate (Fig. 3).

An important anthropogenic input to the Coastal Aquifer is artificial recharge (injection), particularly from the National Water Carrier, which originates

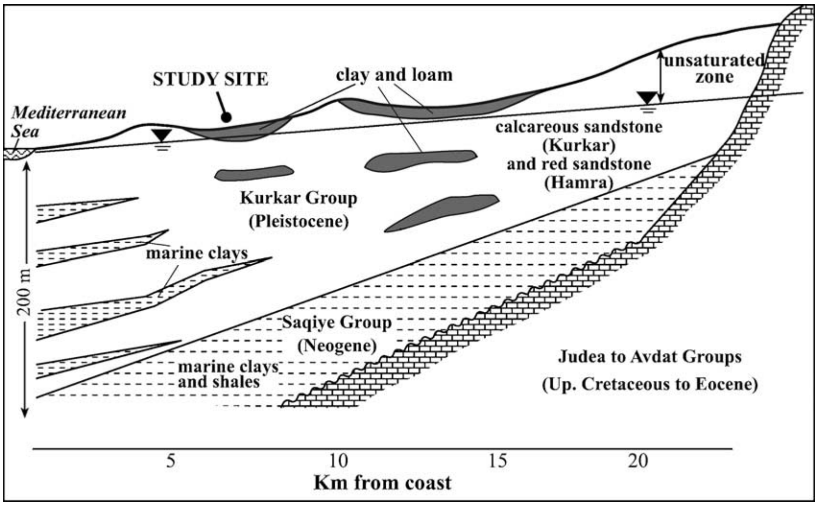

Fig. 2. Schematic geological cross section of the Israeli Coastal Plain.

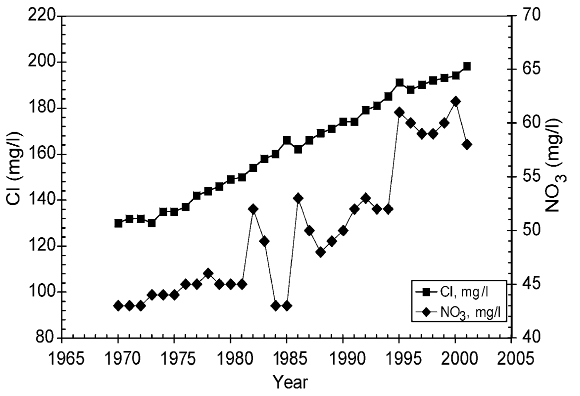

Fig. 3. Nitrate and chloride average concentration in the Coastal Plain between 1970–2000 (data from Israel Hydrological Service, calculated from predetermined wells which are assumed to represent the entire Coastal Aquifer).

from the Sea of Galilee (200–250 mg/l Cl). The artificial recharge of the aquifer began in the 1960s and is most intensive during rainy winters when water from the Sea of Galilee is pumped out to make storage space for inflowing water. Beside the higher salinity of the injected water it is also characterized by a more isotopically enriched oxygen composition and different ionic ratios (e.g. lower Na/Cl ratio; Vengosh et al., 1999).

A dramatic increase in irrigation with treated wastewater has occurred over the last decades, reaching about 250 million cubic meters (MCM) in the 1990s (Tarchitzky et al., 2001). The chlorinity of most sewage effluents in Israel ranges between 170 and 360 mg/l Cl, depending on the specific source and is generally characterized by Na/Cl (molar ratio) >1 and relatively high SAR (>4; Sodium adsorption ratio: $m\mathrm{Na}/\sqrt{(m\mathrm{Ca}+m\mathrm{Mg})}$). Much of the irrigation with wastewater on top of the Coastal Aquifer is done in agricultural fields located in troughs between Kurkar ridges under the assumption that the thick clayey sediments would limit the infiltration of the irrigating water and their salts to the groundwater below. The effectiveness of this configuration in preventing salinization of the groundwater below has never been studied. The objectives of this investigation are to study groundwater impacted by irrigation in the Coastal Plain, to assess the above assumptions, and to evaluate the processes that impact the groundwater quality at the WTR and their relation to the regional aquifer.

2. Methods

The study area is located in the fields of Kibbutz Nitzanim, between Ashkelon and Ashdod, in the southern part of the Coastal Aquifer (Fig. 1). The agricultural fields in the study area are located in a clayey trough, between two sandy ridges. Most fields have been cultivated for over 40 years, though no precise record is available regarding the crops, irrigation methods or application rates. Some of the fields in this area have a long record of irrigation with wastewater (over 20 years) (termed hereafter 'wastewater field') while adjacent fields were only irrigated with freshwater ('freshwater field') derived from pumping regional groundwater (Kibbutz Nitzanim A and B wells). Most common crops grown include corn, cotton, sunflowers, chick-pea and wheat. Irrigation initially was by sprinklers but more recently and depending on the nature of the crops, it is through dripping systems. The fields are irrigated mainly during the summer months and the overall amount of water applied to the field is estimated at 500 mm/yr, roughly the equivalent of the local annual precipitation. The use of drip irrigation or night sprinkle irrigation are important practices in water saving and minimize water loss by evaporation and/or rapid penetration of water below the root zone.

2.1. Research wells and sampling

Seven research wells were drilled in the study area in the fields of Kibbutz Nitzanim. Well NTZ-3 was drilled at the center of the wastewater field to the WTR and was replaced 2 years later by well NTZ-8 after the former dried out due to regional water level drop. Well NTZ-4 was drilled in the eastern edge of the same field, at the eastern border of the clayey trough. Well NTZ-5 was drilled in a non-irrigated field on the western border of this trough, only 50 meters away from the border of the wastewater field. NTZ-6 was drilled in a freshwater field in a center of an adjacent trough. All the above wells were drilled to a depth of about 25–27 meters, 3–5 m below the water table. A single well, NTZ-7 located adjacent to NTZ-3 and NTZ-8, was drilled to a depth of 40 m, nearly 20 m below the water table. The drilling was done by a rotary drill without drilling mud or water.

The boreholes were outfitted with 2" or 3" diameter PVC tubes and the annular space around the screens was packed with washed quartz sand. Some of the boreholes were plugged with cement above the screens to avoid contamination from above. The completed boreholes were purged by pumping for 1–2 h, and were left to equilibrate with regional groundwater for at least 4 weeks before sampling.

Water samples from the research wells were collected with a hand sampler or a submersible pump several times over the 4 year study period (1997–2001). Water temperature and pH were measured in the field. In several boreholes we preformed detailed depth profiles using a Multi Layer Sampler (MLS), which allows sampling resolution of 10 cm (Ronen et al., 1987). The MLS was allowed to equilibrate with the local groundwater for over 2 months before it was pulled out from the boreholes and its water collected for analyses. The wastewater used for irrigation was sampled from the oxidation pond of Kibbutz Nitzanim. The regional aquifer was sampled from pumping wells in the immediate surroundings of the research site.

2.2. Chemical and isotopic analyses

Upon sampling in the field, samples were ice packed, and transferred to the GSI within few hours where they were stored in refrigerators at 4 °C. Chemical analyses of water samples were conducted in the laboratories of the Geological Survey of Israel (GSI) as follows: Na, K, Mg, Ca, Sr, SO_4, B, by inductively coupled plasma atomic emission spectrometer (ICP-AES: Perkin-Elmer, Optima 3000), HCO_3 by titration, Cl, Br and NO_3 by ion chromatography (Dionex-4000i), all with analytical reproducibility better than $\pm 2\%$ (Kafri et al., 2002). Oxygen and hydrogen isotope compositions were determined with a VG Sira-II mass spectrometer following Epstein and Mayeda (1953) and Coleman et al. (1982) with analytical reproducibility of $\pm 0.1‰$ and $\pm 1‰$, respectively. Tritium analyses were conducted in the Weizmann Institute of Science. The water samples were first enriched by electrolysis and then mixed with scintillation liquid and measured in a Wallac 1220 scintillation counter (Kaufman et al., 2003). Analytical uncertainty of tritium analyses is ± 0.4 tritium units (T.U.).

3. Results

3.1. Hydrogeology

The location of the boreholes and their schematic geological setting are illustrated in Figs. 1 and 4, respectively. Fig. 4A includes also chloride concentration and other geochemical parameters encountered at the WTR and the nearby regional groundwater. Elevation of the studied agricultural fields is 24–28 m above mean sea level and depth to the water table was 21–24 m. Elevation of the water table was found to be similar to that of the regional water level as measured in pumping wells in the vicinity of the study area. The four years duration of the study period were characterized by regional water level declined due to over-pumping. This decline was also detected in the research wells, further confirming the hydraulic continuity of the WTR in the studied area with the regional aquifer. During the drilling operation no indication for confined conditions were detected, showing that the aquifer beneath and within the clayey trough remains phreatic. The lithological section in the center of the wastewater field (NTZ-3, 7 and 8) and the freshwater field (NTZ-6) consist of clayey sand and sandy clay sediments to a depth of about 29 m. Below 29 m the aquifer is composed mainly of calcareous sandstone and sandy sediments (well NTZ-7) with few clayey horizons. Below the eastern and western edges of the trough, the clayey sediments are limited to the upper part of the section and the WTR is located within sands or calcareous sandstones (wells NTZ-4 and NTZ-5, respectively, Fig. 4A).

NTZ-4 was drilled on the eastern border of the wastewater field, only ~20 m from Gat-23 well. Because of its location, this site is not always part of the agricultural field, and is irrigated only during those years that it is included within the cultivated field. During the study period its immediate surrounding was not irrigated. NTZ-5 was drilled in a non-irrigated field which nevertheless is cultivated and fertilized. It is located several tens of meters from the western border of the wastewater field. Except for the one meter of the upper soil, the entire section here consists of sand. In NTZ-7, the deepest borehole drilled in the framework of the study, the screen was installed below the clayey sediments of the trough, within the sand and calcareous sandstone of the aquifer, at a depth range from 34 to 37 m.

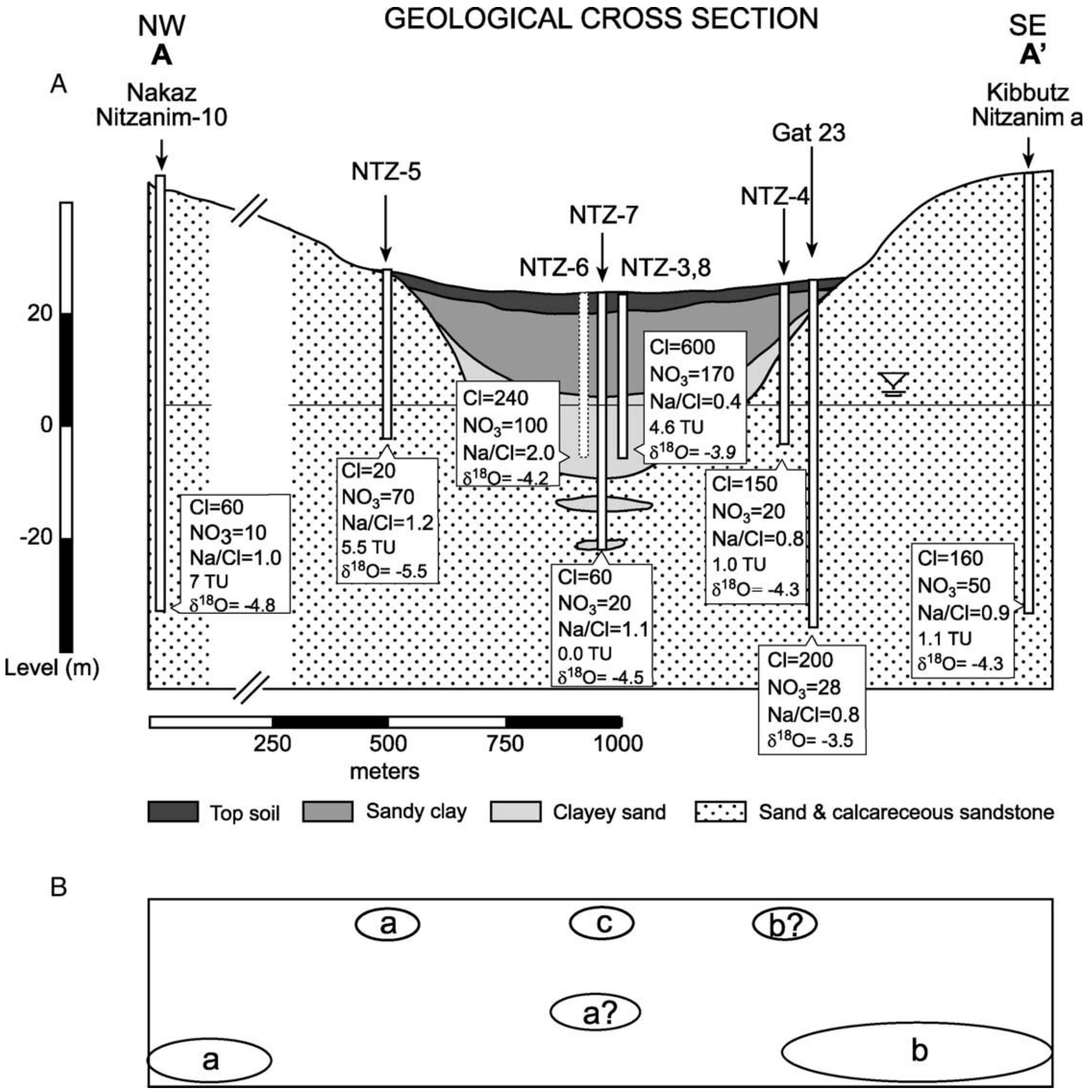

Fig. 4. (A) A schematic geological cross section in the study area (A–A′ in Fig. 1), including nitrate and chloride concentrations (mg/l), $\delta^{18}O$ (‰), and tritium (TU) values and Na/Cl ratios in groundwater. Note that well NTZ-6 is superimposed on the cross section based on its morphological location and lithology. (B) Schematic spatial representation of the different water types found in the present study: (a) High quality-low salinity waters of the Nakaz wells in the west of the aquifer, derived from rapid recharge through the sand dunes. Water of NTZ-7 could have flowed eastward due to overpumping in the 1960–70. (b) Higher salinity water of the Gat wells, east of the Nakaz area. NTZ-4 water may represent similar water. (c) High salinity/high nitrate water recharging at irrigated fields (wastewater and freshwater irrigation) through the clayey troughs.

3.2. Chemical and isotopic compositions of groundwater

The groundwater collected from pumping wells (Table 1) and research boreholes (Table 2) show a wide range of salinities and chemical compositions, ranging from very fresh groundwater (∼20 mg/l Cl), to nearly brackish (∼600 mg/l Cl; Fig. 4A). The Na/Cl molar ratio varies between 0.4 and 2.0. A very large variability was also found in the nitrate concentrations, ranging from 20 to 170 mg/l. The $\delta^{18}O$ composition of the water ranges between −5.5 and −3.5‰

Table 1
Chemical and isotopic compositions of pumping wells in the study area

Well	Date	$\delta^{18}O$ (‰)	δD (‰)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Sr (mg/l)	Cl (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	NO_3 (mg/l)	Br (mg/l)	TDS (mg/l)	Na/Cl (eq/eq)	K/Cl (eq/eq)	Ca/Cl (eq/eq)	SO_4/Cl (eq/eq)	NO_3/Cl (eq/eq)	HCO_3/Cl (eq/eq)
Western Wells (Nakaz Wells)																				
Nitzanim 1	15/06/1998	−4.6	−19.0	70	1.8	81	31	1.3	158	30	263	32	0.5	666	0.68	0.010	0.91	0.14	0.12	0.97
Nitzanim 2	15/06/1998	−4.5	−18.0	65	2.1	68	30	1.1	120	24	268	25	0.3	602	0.83	0.016	1.00	0.15	0.12	1.30
Nitzanim 3	15/06/1998	−4.6	−17.0	48	3.9	52	21	0.8	69	14	240	16		463	1.08	0.052	1.34	0.15	0.13	2.04
Nitzanim 3	31/08/1999			58	4.0	51	23	0.8	73	17	251	17	0.2	493	1.23	0.050	1.25	0.17	0.14	2.01
Nitzanim 4	15/06/1998	−4.7	−21.5	38	2.3	43	16	0.6	54	12	205	12		383	1.09	0.039	1.41	0.16	0.12	2.20
Nitzanim 4	31/08/1999			48	2.6	44	18	0.7	58	14	215	12	0.2	411	1.28	0.041	1.32	0.17	0.12	2.14
Nitzanim 5	15/06/1998	−4.7	−19.0	47	4.4	49	17	0.6	69	15	222	11		433	1.04	0.058	1.25	0.16	0.09	1.87
Nitzanim 5	31/08/1999			56	5.0	48	19	0.7	71	16	232	13	0.2	459	1.22	0.064	1.21	0.17	0.10	1.91
Ntz 11 NK	15/06/1998	−4.8	−20.0	48	2.3	48	19	0.6	54	14	254	10		448	1.36	0.038	1.58	0.19	0.10	2.72
Ntz 11 NK	22/11/1999			56	2.5	55	20	0.7	64	17	273	10	0.2	498	1.35	0.036	1.52	0.19	0.09	2.48
Ntz 10 NK	15/06/1998	−4.8	−21.5	38	2.0	52	15	0.6	56	11	234	8		416	1.04	0.033	1.64	0.15	0.08	2.44
Ntz 10 NK	22/11/1999			40	2.1	56	16	0.6	60	14	229	8	0.2	425	1.03	0.031	1.65	0.17	0.08	2.22
Ashdod Yam 2	15/06/1998	−4.7	−20.0	59	1.8	70	31	0.9	100	40	278	32	0.3	612	0.91	0.016	1.25	0.30	0.18	1.62
Ashdod 3	22/11/1999			56	1.4	50	22	0.7	74	17	261	16	0.2	498	1.17	0.017	1.20	0.17	0.12	2.05
Ashdod 4	22/11/1999			68	1.2	53	23	0.7	86	19	259	16	0.3	524	1.22	0.012	1.09	0.16	0.11	1.75
Eastern Wells (Gat Wells)																				
Kibbutz Nitz. B	15/06/1998	−4.3	−17.0	84	2.0	69	41	1.3	155	32	276	53	0.6	710	0.84	0.012	0.78	0.15	0.19	1.03
Kibbutz Nitz. B	12/07/1998			84	2.0	66	40	1.2	162	31	276	57	0.6	718	0.80	0.011	0.72	0.14	0.20	0.99
Kibbutz Nitz. A	15/06/1998	−4.4	−22.0	107	4.2	70	46	1.4	182	34	322	53	0.6	818	0.90	0.021	0.68	0.14	0.17	1.03
Kibbutz Nitz. A	12/07/1998			110	4.6	68	46	1.4	196	32	325	56	0.6	838	0.87	0.021	0.62	0.12	0.16	0.96
Kibbutz Nitz. A	22/11/1999	−4.2		114	3.9	74	46	0.1	191	39	329	47	0.6	844	0.92	0.019	0.69	0.15	0.14	1.00
Kibbutz Nitz. A	06/04/2000	−4.2		115	3.6	74	46	1.5	192	39	327	52	0.6	849	0.92	0.017	0.69	0.15	0.15	0.99
Gat 1	15/06/1998	−3.8	−15.0	85	4.2	120	34	1.2	238	77	234	41	0.9	833	0.55	0.016	0.89	0.24	0.10	0.57
Gat 3	15/06/1998	−4.3	−17.0	87	2.5	101	39	1.4	220	58	252	48	0.8	809	0.61	0.010	0.82	0.20	0.12	0.67
Gat 5	15/06/1998	−4.3	−17.0	140	2.7	72	50	1.5	270	42	320	32	0.8	928	0.80	0.009	0.47	0.11	0.07	0.69
Gat 6	15/06/1998	−4.1	−16.5	114	3.7	69	43	1.2	186	33	337	38	0.5	823	0.95	0.018	0.65	0.13	0.12	1.05
Gat 7	15/06/1998	−3.6	−16.5	109	7.3	86	43	1.2	196	51	320	64	0.9	877	0.86	0.034	0.77	0.19	0.19	0.95
Gat 9	15/06/1998	−4.5	−18.5	119	2.0	66	38	1.2	182	35	323	33	0.5	798	1.01	0.010	0.64	0.14	0.10	1.03
Gat 21	22/11/1999			114	4.9	79	35	0.9	225	58	262	31	1.1	809	0.78	0.020	0.62	0.19	0.08	0.68
Gat 22	15/06/1998	−3.7	−16.5	124	3.1	110	37	1.2	280	56	273	43	1.1	926	0.68	0.010	0.69	0.15	0.09	0.57
Gat 23	22/11/1999	−4.0		111	3.8	72	40	0.1	214	45	281	33	0.9	800	0.80	0.016	0.60	0.16	0.09	0.76
Gat 24	15/06/1998	−3.9	−16.5	157	3.0	57	39	1.1	226	50	322	31	0.8	886	1.07	0.012	0.45	0.16	0.08	0.83
Gat 25a	18/01/2000	−3.3	−12.5	120	5.0	64	34	0.9	208	52	232	9	1.5	724	0.89	0.022	0.55	0.19	0.03	0.65

Table 2
Chemical and isotopic compositions of water in the WTR in the NTZ research wells and the wastewater used for irrigation

Well and sampling method	Date	Meters below water table	$\delta^{18}O$ (‰)	δD (‰)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Sr (mg/l)	Cl (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	NO_3 (mg/l)	Br (mg/l)	NH_4 (mg/l)	TDS (mg/l)	Na/Cl (eq/eq)	K/Cl (eq/eq)	Ca/Cl (eq/eq)	SO_4/Cl (eq/eq)	HCO_3/Cl (eq/eq)	NO_3/Cl (eq/eq)
NTZ 3 (center of wastewater field)																						
Hand sampler	18/11/1998	0.5	−4.0	−16.5	126	4.2	179	123	3.7	514	64	315	170	2.1		1494	0.38	0.007	0.62	0.09	0.36	0.189
Pumping	18/11/1998		−3.8	−15.0	146	2.5	187	129	3.9	565	62	332	181	2.3		1604	0.40	0.004	0.59	0.08	0.34	0.183
Hand sampler	26/01/1999	1.0	−3.9		133	2.7	173	119	3.6	556	69	303	186	2.0		1541	0.37	0.004	0.55	0.09	0.32	0.191
Hand sampler	28/07/1999	2.5	−3.6		135	2.5	181	123		515	57	303	162	2.6		1478	0.40	0.004	0.62	0.08	0.34	0.180
NTZ 8 (center of wastewater field) − replaces well NTZ-3 which dried out following water level drop and technical problems																						
Pumping	31/07/2000				181	3.5	259	96	3.3	514	193	439	147	1.8		1833	0.54	0.006	0.89	0.28	0.50	0.164
Before pumping	23/10/2000		−4.0		160	3.0	228	122	4.5	598	63	390	180	2.4		1744	0.41	0.005	0.68	0.08	0.38	0.172
During pumping	23/10/2000				158	2.8	219	112	3.7	572	54	401	170	2.2		1688	0.43	0.004	0.68	0.07	0.41	0.170
End of pumping	23/10/2000		−3.8		157	2.7	215	108	3.6	547	49	408	165	2.2		1652	0.44	0.004	0.70	0.07	0.43	0.172
nTZ 7 (deep well in the center of wastewater field)																						
During drilling	16/07/2000	17.0	−4.7		52	1.6	39	21	0.8	74	20	193	23	0.3		424	1.08	0.019	0.93	0.20	1.51	0.179
During drilling	16/07/2000	19.0			41	1.2	43	24	0.8	60	15	217	22	0.3		423	1.05	0.018	1.25	0.19	2.09	0.213
During drilling	17/07/2000	17.0	−4.5		45	1.3	36	20	0.7	68	19	174	19	0.3		381	1.03	0.018	0.95	0.20	1.49	0.161
Pumping	23/07/2000				40	1.4	42	20	0.7	58	40	178		0.2		378	1.07	0.022	1.29	0.51	1.79	
NTZ 4 (East side of wastewater field)																						
Hand sampler	15/11/1998	2.5	−4.4	−16.5	106	16.0	96	43	1.4	208	15	421		0.8		904	0.79	0.070	0.82	0.05	1.18	
Hand sampler	26/01/1999	1.0	−3.9		95	16.2	100	34	1.2	204	24	373	16	0.7		861	0.71	0.072	0.86	0.09	1.06	0.045
Hand sampler	30/06/1999	1.0	−4.6		72	18.5	91	26	0.1	131	20	337	30	0.5		724	0.84	0.128	1.23	0.11	1.49	0.132
Pumping	28/07/1999		−4.5		84	17.5	96	22	0.8	152	22	307	30	0.6		731	0.85	0.104	1.11	0.11	1.18	0.113
Hand sampler	18/01/2000	1.0	−4.3		80	17.0	96	21	0.8	143	23	303	30	0.7		713	0.86	0.108	1.19	0.12	1.23	0.120
NTZ 5 (Non-irrigated field, west of wastewater field)																						
Hand sampler	15/11/1998	1.0	−5.5	−23.0	15	9.7	109	13		22	10	304	67	0.2		548	1.03	0.403	8.82	0.35	8.10	1.750
Hand sampler	26/01/1999	3.0	−5.2		17	1.0	104	13	0.5	26	26	298	66	0.1		551	1.02	0.035	7.20	0.74	6.76	1.481
Hand sampler	30/06/1999	2.5	−5.7		16	1.0	99	13	0.5	22	23	287	67	<0.1		528	1.14	0.043	8.10	0.78	7.69	1.758
Hand sampler	18/01/2000	2.0	−5.3		16	0.9	113	14	0.6	22	22	296	64	0.1		548	1.07	0.034	8.94	0.74	7.69	1.634
NTZ 6 (center of freshwater field)																						
Pump	18/01/2000		−4.8		284	3.3	128	60	1.5	226	112	769	102	0.9		1683	1.94	0.013	1.00	0.37	1.98	0.258
Hand sampler	06/04/2000		−4.2		298	3.4	116	57	1.5	238	110	778	105	1.3		1705	1.93	0.013	0.86	0.34	1.90	0.252
Hand sampler	06/04/2000		−4.1		301	3.5	116	56	1.5	238	115	761	105	1.3		1695	1.95	0.013	0.86	0.36	1.86	0.252
Hand sampler	20/08/2001				345	3.5	97	54	1.2	220	115	834	96	0.9		1765	2.42	0.014	0.78	0.39	2.20	0.250
Nitzanim Wastewater																						
Waste water	05/07/1998				203	24.7	55	34	1.1	256	24	487	1	0.7		1084	1.22	0.087	0.38	0.07	1.11	0.002
Waste water	23/06/1998				203	24.7	55	35	1.0	281	31	401	0.3	0.7		1031	1.11	0.080	0.35	0.08	0.83	0.001
Waste water	29/11/1999				224	23.1	58	40	1.1	270	35	610	0.6	0.6	46	1260	1.28	0.078	0.38	0.10	1.31	0.001
Waste water	15/12/1999				193	21.3	53	35	0.9	232	35	537	<0.3	0.5	35	1105	1.28	0.083	0.40	0.11	1.34	

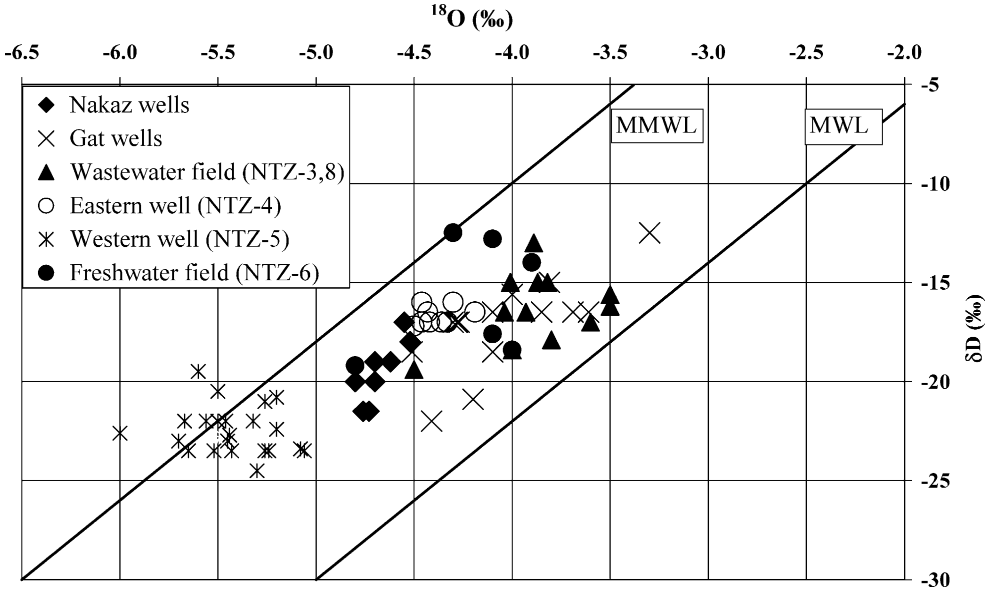

Fig. 5. $\delta^{18}O$ vs. δD in the research and pumping wells. MWL: Global Meteoric Water Line (Craig, 1961); MMWL: Mediterranean Meteoric Water Line (Gat and Dansgaard, 1972).

and the tritium range between 0 and 7 T.U. In fact, under the center of the wastewater field, the tritium content varies as a function of depth, with 0 TU at 37 m (Well NTZ-7) vs. 4.6 T.U. at 23 m (Well NTZ-8). Water temperature and pH values in all wells varied in the ranges of 23–24 °C and 7.1–7.7, respectively. Saturation index (SI) calculation using PHREEQC indicate that the water at the WTR below the irrigated fields are saturated to oversaturated with respect to calcite ($SI \approx 0.5$). This is in line with the abundant calcite in the aquifer and unsaturated zone above. Most of the water in the aquifer is also saturated except in the Nakaz wells where it is slightly under-saturated ($SI \approx -0.2$).

Fig. 5 plots the $\delta^{18}O$ vs. δD values of the groundwater in the studied area. Most of the data points fall between the local Mediterranean Meteoric Water Line (MMWL; Gat and Dansgaard, 1972)

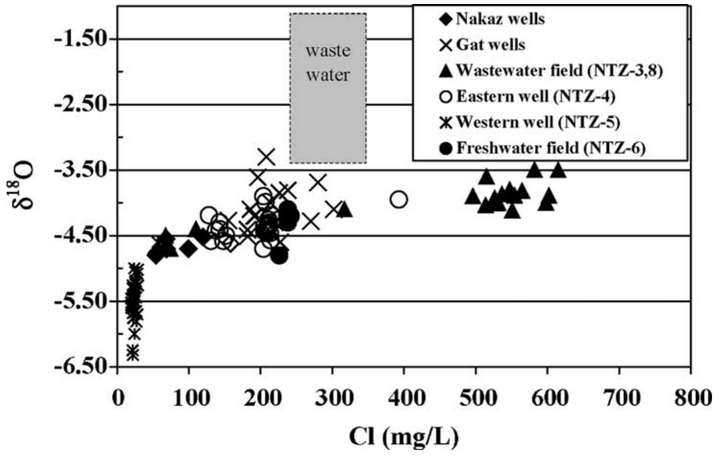

Fig. 6. $\delta^{18}O$ vs. Cl concentration in the research and pumping wells (range of wastewater composition after Vengosh et al., 1999).

and the global Meteoric Water Line (MWL, Craig, 1961), except for few samples from NTZ-5, which fall on, or even above, the MMWL. The deviation of the Gat wells from the MMWL indicates that either the water has experienced some degree of evaporation relative to the local rain, or that it contains some isotopically enriched water from the Sea of Galilee. The plot of δ^{18}O vs. Cl concentrations (Fig. 6) shows that the relationship between the salinity and δ^{18}O is not simple. The range presented for wastewater in Fig. 6 (−3.4 to −1.3‰) is taken from Vengosh et al. (1999) based on wastewater composition in oxidation ponds in the vicinity of the study area.

3.3. Detailed chemical profiles of groundwater sampled by the multi level sampler

Detailed chemical depth profiles in the WTR were obtained by the MLS device. Profiles were collected from well NTZ-6 (3 profiles in freshwater field; Aug. 2000, Oct. 2000, and Mar. 2001) and well NTZ-8 (a single profile in wastewater field, Oct. 2000). Most ions display homogenous depth profiles that are in agreement with the values obtained from samples collected by the conventional methods of pumping or bailing. This is well illustrated by the Cl profile (Fig. 7a). Particular large variation was found in the profiles of the SO_4 collected from NTZ-8 and from the two later profiles from NTZ-6 which exhibit a decreasing concentration with depth (Fig. 7b). The SO_4 concentration decreases within the 3 m range of the sampling by nearly 50%, while the NO_3 concentrations exhibit an opposite trend. It should be noted that in both NO_3 and Cl profiles of NTZ-8, the uppermost samples exhibit large variations relative to the rest of the profile.

3.4. Wastewater

The wastewater used for irrigation of the study field was sampled from an open oxidation pond reservoir several times during the course of the study (Table 2) and had chloride concentration of ~270 mg/l and Na/Cl molar ratio of 1.2. As typical for wastewater, the NO_3 concentration is very low (<1 mg/l) while the water contains high levels of ammonium (40 mg/l; 2.2 meq/l). The historical data on the wastewater composition obtained from Kibbutz Nitzanim shows that during the summer months, when most of the irrigation takes place, there is little variability in the Cl concentration. Due to technical problems, the oxygen isotope composition of the wastewater was determined only on a single wastewater sample. The value obtained (−3.0‰) falls within the range of compositions given by Vengosh et al. (1999) for wastewater in open oxidation ponds in the region (−3.4 to −1.3‰).

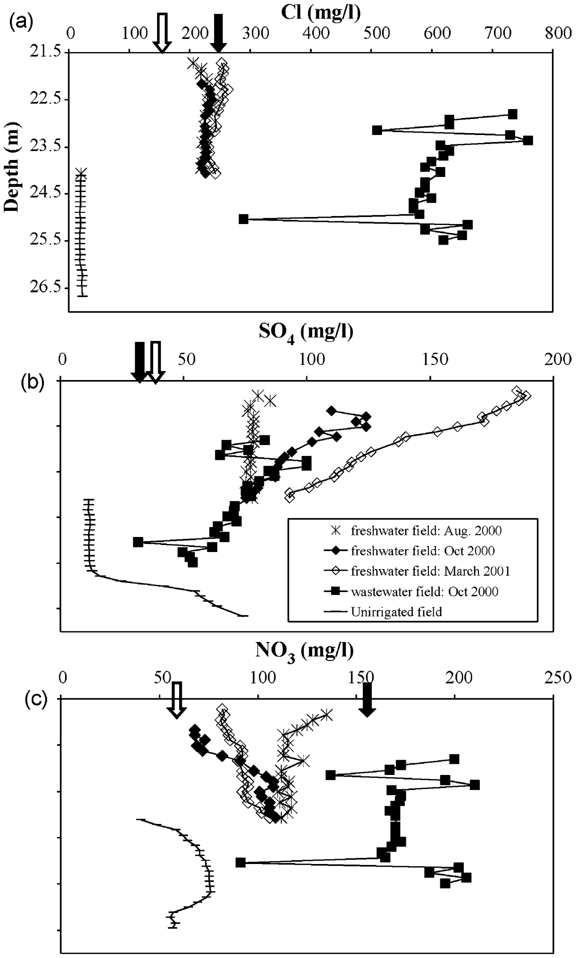

Fig. 7. Profiles obtained by MLS sampling of the research wells. (a) chloride, (b) sulfate, (c) nitrate. Hollow arrow: composition of freshwater used for irrigation. Full arrow: Wastewater composition.

4. Discussion

The data collected in the present study shows a very high spatial variability in water composition and salinity in the WTR over very short distances of only few hundred meters. The highest salinity encountered in the WTR is below the wastewater-irrigated field. This suggests a significant salt contribution from the irrigation water to the aquifer and supports the common argument that wastewater irrigation has the potential to accelerate salinization rates of underlying phreatic aquifers. Yet, the chemical compositions of the WTR water below the wastewater-irrigated field and the freshwater-irrigated field, are distinctly different from the respective irrigating waters. In order to associate the irrigating waters with the underlying groundwater, chemical modifications via interaction with the unsaturated zone (e.g. Mitchel et al., 2000; DeSimone et al., 1997) must be identified. These reactions, which will be discussed hereafter, imply that there is not a simple relationship between the compositions of irrigation waters and the contaminated groundwater below.

In the following discussion, the geochemistry of the deeper, regional groundwater is treated separately from the processes at the WTR.

4.1. Regional groundwater

Distinct differences in the chemical and isotopic compositions exist between groundwater in the western part (the Nakaz and Nitzanim wells) and eastern part (Gat and Kibbutz Nitzanim wells, Fig. 4A and B) of the Coastal Aquifer near the study area. The western-most part of the aquifer is characterized by relatively low salinity and a somewhat more depleted oxygen isotopic composition relative to the water to the east (Fig. 4A; Table 1). These are best explained by differences in water sources and recharge history. The groundwater in the east had during the 1960's a typical salinity of <180 mg/l Cl and Na/Cl>1 (1.1–1.2). The salinity increase over the last decades was accompanied by a decrease in the Na/Cl ratio from that which characterizes weathering of siliceous minerals in the aquifer. The present Na/Cl ratio (0.8–0.9) can at least partly be attributed to artificial recharge of water from the Israeli National Water Carrier (Vengosh et al., 1999; Velder, 2003). The latter was mainly pumped from the Sea of Galilee, which has distinctly higher salinity (220 to 300 mg/l Cl) and different chemical (Na/Cl = 0.75) and isotopic composition ($\delta^{18}O \approx -1$‰). However, some of the Gat wells have Na/Cl ratios below that of the Kinneret water and therefore additional processes and/or sources must account for this modification in composition over the last decades. As will be shown later, recycling of salts due to irrigation by wastewater could account for this change.

In contrast to the Gat wells area, the original low salinity and high Na/Cl ratios of groundwater in the western part of the aquifer (Nakaz wells) did not change significantly during the past decades, implying that this part of the aquifer is less susceptible to anthropogenic influence. The high quality of the Nakaz water can be attributed to two factors: (1) No major agricultural or other human activity takes place above the aquifer in the immediate vicinity of the wells, and (2) the nature of the unsaturated zone, which consists mainly of uncemented sand, enables efficient recharge and rapid flushing of this part of the aquifer with no salt accumulation in the unsaturated zone.

The oxygen isotope compositions of the eastern and western areas also reflect the sources of water. The composition of the aquifer in the Gat boreholes is isotopically enriched ($\delta^{18}O \approx -4.0$‰; Table 1) compared to local rain (-6.0 to -5.0‰; Gat, 1981). This is best explained by the effect of evaporation prior to recharge of rainwater, which in the Israeli Coastal Plain was estimated to be on the order of 1‰ (Gat, 1981). The deviation of these waters from the MMWL (Fig. 5) is in accordance with such evaporation process. Contribution from the artificial recharge of National Water Carrier water ($\delta^{18}O < -1$; Vengosh et al., 1999) could account for the more isotopically enriched compositions in some of the wells (e.g. Gat 25a, $\delta^{18}O = -3.3$‰; Table 1). It should be emphasized that summer irrigation, if managed correctly so that all the water is consumed by the growing crops, should not contribute water to the groundwater and therefore should have no impact on its isotope composition. The more depleted $\delta^{18}O$ values in the Nakaz wells (-4.7‰) provide further evidence for the efficient recharge and therefore limited evaporation over the western-most part of the aquifer, where the soil cover is minimal to non-existent. Such recharge would not allow salt accumulation in the unsaturated zone. Indeed, on the $\delta^{18}O$–δD graph (Fig. 5), these water are found closer to the MMWL, indicating more limited evaporation.

The increase with time in the NO_3 content of the groundwater in the aquifer (Fig. 3) is commonly attributed to the agricultural activity on top (Ronen et al., 1983). Indeed, in the Gat wells, located in intensely cultivated area, the NO_3 concentration varies within the range of 30–60 mg/l. In contrast, in the western-most part of the aquifer, little, if any, such activity exists and the NO_3 concentration in most of the Nakaz wells remain relatively low (<16 mg/l). Nevertheless, it should be noted that despite the generally high quality of the Nakaz wells, some degradation in water quality occurs here too. Nitzanim 1 and Nitzanim 2 wells, located in the southwestern part of the study area, show increased Cl and NO_3 concentration and low Na/Cl ratio as compared to the other Nakaz wells, suggesting that some groundwater from the eastern part of the aquifer have reached this part of the aquifer.

The deep research well (NTZ-7) drilled in the center of the wastewater field exhibits a very low salinity at its bottom, and is rather similar in composition to the Nakaz wells (Fig. 4). Its composition indicates that the impact of wastewater irrigation, identified at shallower depth (NTZ-3, 8; see hereafter), has not yet reached the deeper and sandy part of the aquifer. In fact, the relatively low NO_3 content and high Na/Cl ratio (1.1), typical to the pristine coastal aquifer, suggests no anthropogenic input. This is further supported by the absence of tritium (0.0 T.U.), indicating an apparent age of >50 years. The location of such relatively old and low-salinity water only few hundred meters from the Gat wells is rather surprising. Two possible explanations for this water can be suggested: (a) The water originated from the Nakaz area, few km to the west and flowed eastward due to over-pumping in the 1960s–1980s and the creation of hydrological lows within the aquifer, which existed also in Nitzanim area. (b) A relatively small water body with limited hydraulic connection to the main aquifer which therefore flows and recharges slower than the rest of the aquifer. However, its water level, which is similar to that of the other research wells and is consistent with the regional water level indicate that it is still part of the aquifer. Detailed study and additional drill holes are required to resolve the history of this interesting water body within the aquifer.

4.2. Groundwater at the water table region

The large chemical differences between the irrigating waters (wastewater and freshwater) and their respective underlying groundwater at the WTR, suggests that major chemical processes take place in the unsaturated zone during the infiltration from the surface toward the water table (Fig. 8). In order to understand these processes we assume that Cl is a conservative element in the studied system (i.e., no sinks or sources), and therefore can be used as a reliable parameter to measure the salinity increase. The primarily process that controls the water salinity in the soil is evapotranspiration, which occurs in the upper part of the unsaturated zone. The enrichment factor between the wastewater and the underlying groundwater at the WTR is ~ 2 (from 280 to 550 mg/l Cl) and in the freshwater field the enrichment factor is 1.3–1.5 (160–190 to 240 mg/l Cl). These rather similar values indicate that the salinization processes due to evapotranspiration in the two fields are comparable.

4.2.1. Base exchange

Together with overall salinization of the underlying groundwater, we observed significant changes in the chemical compositions. The groundwater underlying the wastewater field displays a significant decrease in the Na/Cl ratio (from 1.2 to ~ 0.4) and increase in the Ca/Cl ratios (from 0.2 to 0.3) relative to those in the irrigation water. In contrast, in the groundwater underlying the freshwater field the Na/Cl (~ 2.0) and Ca/Cl (0.4) ratios are higher than those in the irrigating freshwater (0.9 and 0.3, respectively). In addition, the groundwater underlying the freshwater field has relatively high HCO_3/Cl and SO_4/Cl ratios (Fig. 8).

Most of the chemical modifications observed are attributed to base-exchange reactions in the unsaturated zone below the irrigated fields. These processes are primarily controlled by the initial SAR and salinity of the irrigating water. Domestic wastewater in Israel is characterized by high Na concentration and high SAR values (>4; Tarchitzky et al., 2001). Such water, when used for irrigation will lead to base exchange whereby Na and K are adsorbed on clay minerals while Ca and Mg are released to the liquid phase (Appelo and Postma, 1993). Indeed, the water

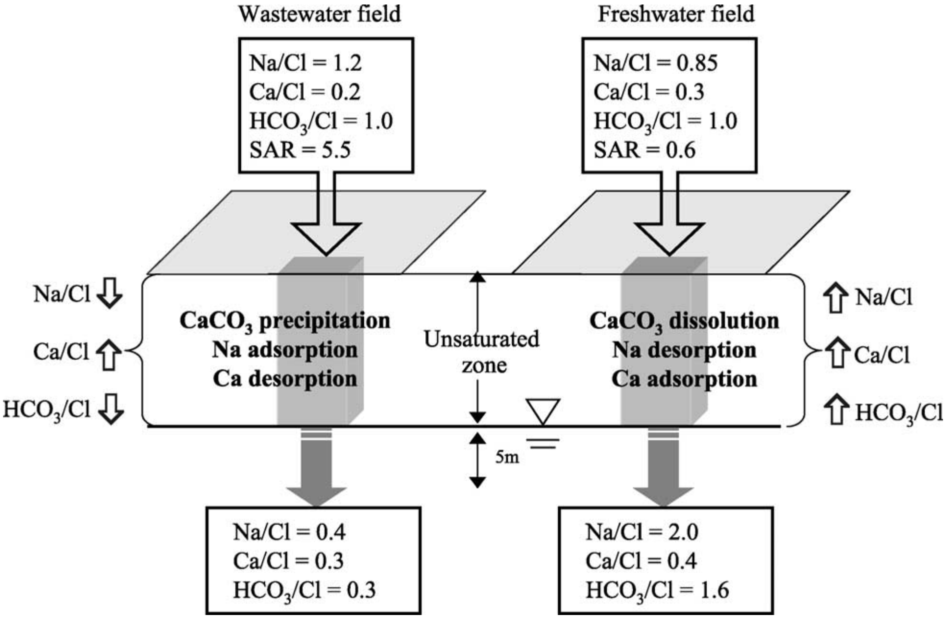

Fig. 8. Schematic representation of the base exchange occurring in the unsaturated zone under freshwater and wastewater fields. ↓: Decrease in ratio; ↑: Increase in ratio.

under the wastewater field displays decreased Na/Cl and K/Cl ratios and higher Ca/Cl ratio compared to the irrigating wastewater (SAR ≈ 3.7–3.9). However, the enrichment of Ca, calculated in equivalent units after correction for evapotranspiration, is much smaller than expected from the decrease in Na concentrations. This and the lowered HCO_3/Cl ratio compared to the wastewater indicate calcite precipitation in the unsaturated zone. Indeed, during the drilling in the wastewater field, white irregular calcite concretions were identified within the clayey sediments. This calcite precipitation is probably triggered by the excess Ca that is released during the base exchange process. Saturation index calculations do indeed indicate that these water are saturated to slightly oversaturated with respect to calcite (SI ≈ 0.5).

The irrigating freshwater over the Coastal Aquifer, which is characterized by relatively low SAR (0.5–0.7) favors exchange reaction opposite to those described for the wastewater. Thus, base exchange drives the Na/Cl ratio in the WTR in the study site to the high value of 2. However, the increased Na/Cl ratio is not accompanied by a corresponding decrease in the Ca/Cl ratio but by a slight increase. We suggest that dissolution of carbonate, which is abundant in the unsaturated zone and in the aquifer, accounts for this increase and would also explain the increase in the HCO_3/Cl ratio. Furthermore, the increase in HCO_3 equivalent concentration is much larger than in Ca, which is in line with the proposed Ca–Na exchange in the unsaturated zone. The dissolution of carbonate in the unsaturated zone could be induced by the exchange reaction which removes Ca from the water. Another driving force for the dissolution would be acidification of the water in the upper soil as it adsorbs CO_2. Such acidification and carbonate dissolution probably occurs also under the wastewater field but the overall exchange reaction and Ca enrichment of the water result in net carbonate precipitation.

The exchange reactions described above are in agreement with previously studies focusing on reactions in the unsaturated zones (e.g. Appelo and Postma, 1993). In fact, Stigter et al. (1998) demonstrated that irrigation with Na-enriched solution values results in ion-exchange reactions: uptake of Na^{+} and release of Ca^{2+} (and Mg^{2+}). In contrast, irrigation with Ca-enriched water releases Na that is bound to the adsorption sites on clay minerals, resulting in high Na/Cl ratios. It is thus anticipated that water recharging the aquifer through the irrigated fields would not maintain the original composition of the irrigating water.

4.2.2. NO_3 and SO_4 behaviors

Nitrogen is not a conservative constituent in water-soil systems. The NO_3/Cl ratio in the WTR under the wastewater field is extremely high relative to that of the wastewater. However, it should be noted that wastewater has no NO_3 but is enriched in NH_4, which may undergo nitrification. In fact, the total nitrogen load in the wastewater, normalized to Cl, is higher than that in the WTR. This suggests that some of the nitrogen is removed from the water in the unsaturated zone, probably through uptake by plants, along with some volatilization, and/or adsorption of NH_4 onto clay minerals. Although NO_3 and NH_4 are not conservative in active cultivated soil systems, the change in the nitrogen concentration between the irrigating water and water at the WTR may be an indication of the differences in the impact of wastewater and freshwater irrigation on the aquifer. The nitrogen concentrations (as NO_3) under the wastewater, although very high (NO_3–N ≈ 170 mg/l), are only enriched by a factor of 1.1 as compared to the irrigating water (where the nitrogen is present as ammonium). This low enrichment indicates an efficient utilization of nutrient from the wastewater. Indeed, fewer commercial fertilizers are applied to fields irrigated by wastewater (B. Kamp, Kibbutz Nitzanim; pers. comm.).

In contrast to the wastewater field, the enrichment factor of NO_3 in groundwater under the freshwater field (1.7) is larger than that of Cl. This indicates that there is an input of nitrate to the aquifer from the agricultural field, additional to that derived from the irrigating water. A likely source for this nitrate source is fertilizers such as $(NH_4)_2SO_4$. Such a source can also account for the increase in the SO_4/Cl in the water at the WTR compared to the irrigating water. Sulfate enrichment in agricultural return flows has also been reported by Vengosh et al. (2002) in Salinas valley, California. Accordingly, the enrichment in SO_4, an ion that is not taken up by the agricultural crops, is much larger than that of NO_3.

The NO_3 concentration under the non-irrigated field (well NTZ-5) exceeds that of chloride and suggests a significant NO_3 enrichment relative to rainwater, which is the major mean by which chloride reaches this field. The source for this NO_3 here must also be fertilizers which are applied to the field even though it is not irrigated.

4.2.3. Oxygen isotopes

The isotope composition of the groundwater underlying the wastewater field ($\delta^{18}O \sim -4‰$) is more depleted than wastewater used for irrigation in the coastal aquifer (> -3.4, Vengosh et al., 1999). This is opposite to the expected trend in most recharging systems, where some evaporation of the recharging water results in isotope enrichment of the groundwater (Gat, 1981). The relatively depleted groundwater below the wastewater irrigated field implies that most of the water, (i.e. H_2O molecules) is not derived from the irrigating wastewater. The source of recharging water must therefore be mainly local precipitation (-6.0 to $-5.0‰$; Gat, 1974) that has undergone some evaporation and isotope enrichment, as indicated by the deviation from the MMWL (e.g. Gat wells, Fig. 5). Thus, the irrigation, which takes place mainly during the dry summer months, supplies the salts to the ground while most of its H_2O evaporates or is uptaken by the plants and transpired. The salts that accumulate in the ground are later dissolved by rainwater that reaches the ground in winter. They are then transported through the unsaturated zone, where the exchange reactions take place, before recharging the aquifer. The same recharge mechanism applies also for the WTR below the freshwater field. Indeed, the similar $\delta^{18}O$ values in the WTR below the freshwater and wastewater fields (-3.9 and $-4.2‰$, respectively, Fig. 4) as compared to the difference in the $\delta^{18}O$ composition of the corresponding irrigating waters (-4.3 and > -3.4, Table 1 and Vengosh et al., 1999) further indicates that only little if any of the actual H_2O from the irrigating water reaches the WTR.

4.2.4. WTR at the eastern border of the clayey trough

The unsaturated zone in well NTZ-4, located on the eastern border of the wastewater field, and near the eastern border of the clayey trough, consists of only several meters of clayey sediments at the top, underlayed by the sandy section which starts several meters above the WTR and forms most of the aquifer. Due to its location, the immediate area is not included within the cultivated field every year. Thus, the salt load derived from irrigation at this site is smaller, and therefore the flux of salt reaching the WTR from directly above can be expected to be limited relative to the center of the field. Nevertheless, the irrigating water here is expected to react similarly with the soil and the clayey sediments in the upper part of the unsaturated section. Yet, the water at the WTR at NTZ-4 is rather similar to that found in the nearby pumping well Gat 23 (Fig. 4a). We propose that this is due to the sandy nature and therefore high hydraulic conductivity at the WTR in this part of the aquifer. The saline water that reach the WTR from above mixes with the main groundwater body of the aquifer faster than the water in the clayey trough below the center of the wastewater field. This mixing process is further enhanced by the pumping activity of the nearby Gat 23 well.

4.2.5. WTR under the non-irrigated field at the western border of the clayey trough

The water at the WTR under the non-irrigated field well (NTZ-5), at the western border of the clayey trough, some 50 m west of the wastewater field, is particularly fresh (Cl ~ 20 mg/l), even fresher than in the Nakaz wells. The low salinity of the water is explained by the combination of (1) no irrigation, (2) unsaturated zone composed nearly entirely of sand, which permits rapid recharge. The isotopic composition of groundwater of this site is depleted (−6.0 to −5.0‰) relative to the overall isotopic range of the aquifer (−5‰ to −4‰; Gat, 1981). On the δ^{18}O–δD graph, the water lie on the Mediterranean meteoric water line (MMWL; Fig. 5), indicating lack of evaporation prior to infiltration and a rapid recharge. Similarly, the Na/Cl ratio in NTZ-5 water is high (1.1), indicating that such composition, typical to siliceous aquifers, is already attained in the unsaturated zone, provided no clayey minerals are present. As discussed above, the relatively high NO_3 content in NTZ-5 well is due to fertilizers that are applied to the non-irrigated fields above.

4.2.6. Detailed chemical profiles of groundwater at the WTR

Detailed water profiles collected by MLS device (Ronen et al., 1987) at the WTR enabled us to study the relationships between the recharging water at the very surface of the WTR and the mixing process with the underlaying groundwater. Homogeneous profiles were found for most ions at the WTR under the wastewater, freshwater and non-irrigated fields (Fig. 7a), indicating that the recharging water, as represented by the topmost MLS samples, has similar concentrations to that of the rest of the WTR. These depth profiles also indicate that down to a depth of a few meters below the water table, mixing with the deeper groundwater has not yet begun. However, the profiles of SO_4 and NO_3 (Fig. 7b and c) suggest that the chemical fluxes of these ions vary with time. Particularly illuminating is the change with time in the SO_4 profile under the freshwater field (well NTZ-6). While the first profile (Aug, 2000) is homogeneous with concentration of about 80 mg SO_4/l, the next profile (Oct. 2000) exhibit increased concentration at the very top, reaching 120 mg SO_4/l. The bottom samples of the profile maintain the previous concentration (80 mg SO_4/l), indicating recharge by SO_4-rich water. A similar but even enhanced process of SO_4-rich recharging water is observed in the following profile (March 2001). The most probable source for the SO_4 in the recharging water is ammonium sulfate ($(NH_4)_2SO_4$) fertilizer, which is occasionally added to the irrigated water. Ideally, the plants would consume the nitrogen while the SO_4 would migrate downwards, reaching the water table in concentrations that represent the fertilization regime. Such a source probably also accounts for the profile under the non-irrigated but fertilized field. However, here sulfate concentration increases at the lower part of the profile. We propose that this profile is due to recent recharge of SO_4-poor water that has little traces of fertilizers. It should be mentioned in this context that sulfate is easily transported to groundwater through the unsaturated zone (e.g. Gvirtzman et al., 1986). Thus, the lower part of the profile is from previous water parcels that recharged the aquifer at this site and contained SO_4 from fertilizers. Accordingly, the SO_4 profiles develop through recharge by different water parcels that represent changes in fertilizer input. Such water parcel model was already suggested by Ronen (1988) for small-scale variations obtained by MLS. The change in the SO_4 content with depth is least pronounced in the wastewater field, probably because fertilizer addition here is minimal.

The NO_3 profiles in NTZ-6 exhibit an opposite trend to those of the sulfate profiles (Fig. 7b and c), which does not agree well with the proposed source of $(NH_4)_2SO_4$ fertilizer. However, while sulfate is derived conservatively by the breakdown of the fertilizer, nitrogen evolution in the unsaturated zone is more complex. The flux of nitrate that is generated in the unsaturated zone is controlled by fertilizer input, but at the same time it is also affected by different removal processes (uptake by plants, volatilization of ammonia, adsorption of NH_4 species on clays). Consequently, the NO_3 profiles obtained with the MLS reflect the changing fluxes of nitrate that reach the WTR.

5. Summary and conclusions

Our study reveals two spatial scales of water quality heterogeneity in the phreatic Coastal Aquifer in Israel; regional variations within the aquifer, and local heterogeneity at the water level region (WTR). The first heterogeneity lies on a scale of several kilometers, whereby regions recharged through sands exhibit low salinity ($\sim$50 mg/l Cl) and depleted $\delta^{18}O$ composition (-6 to -5‰), similar to local rainwater. In contrast, regions that are recharged through soils from which evapotranspiration takes place, are characterized by higher salinity ($\sim$150 mg/l Cl) and somewhat more enriched oxygen isotopic compositions (-5 to -4‰). Other sources of recharge, particularly artificial recharge contribute to the heterogeneity in water composition and salinity of the aquifer. On a local scale, our data show that the chemical composition of shallow groundwater at the WTR depends on combination of three factors; (1) the quality of the source water that recharges the aquifer; (2) the lithology of the unsaturated zone; and (3) modifications processes within the unsaturated zone. These factors can lead to differences in salinity in the WTR of order of magnitude over distance of only a few hundred meters. The most saline water was found at the WTR below the wastewater-irrigated field in a clayey trough as opposed to a nearby sandy agricultural field that is not irrigated (500 and 20 mg/l Cl, respectively).

Our data also reveal that the unsaturated zone acts as a chemical buffer for different water sources. Irrigation with Na-rich, high SAR water, which characterize most domestic wastewater worldwide, disturbs the natural balance of the exchangeable cations and results in Na–Ca exchange whereby Na replaces Ca on the adsorbed sites of clay minerals. In our case study, this leads to a major decrease in the Na/Cl ratio from 1.1 in the wastewater to 0.4 in the groundwater underneath and to calcite precipitation. In contrast, recycling of the aquifer water as a source for irrigation produces an opposite trend. The Ca-rich freshwater water, together with Ca that is released from dissolution of the carbonate matrix of the unsaturated zone, trigger Na release into the liquid phase and a high Na/Cl ratio in the water that recharges into the WTR.

In addition to salinity increase, we observed significant nitrate enrichment in all of the investigated shallow groundwater. Where freshwater is used for irrigation, or under the non-irrigated field, fertilizers could be the major source of this nitrate. In contrast, under the wastewater fields, where much less nitrogen-based fertilizers are applied, the nitrate in the WTR is derived from nitrogen present in the wastewater as NH_4. In fact the N/Cl ratio in the WTR is lower than that in the irrigating wastewater, indicating that some of the nitrogen is removed, probably by plant uptake and adsorption of NH_4 to clay minerals.

Our results show, as expected, a relatively slow water flow from the more clayey to the more sandy parts of the aquifer. This is best exemplified in the wells under the wastewater field, where a change in the water quality with depth coincides with the changes in lithology; from clayey sediments that are occupied by relatively saline groundwater in the upper part towards sandy sediments that contain low salinity groundwater at the bottom. Since the water levels in the research wells match the regional water level, there must be a hydraulic continuity between the clayey trough and the main aquifer. This has important implications for water quality monitoring. Typically, the rate of groundwater contamination is determined by the flow rate in the unsaturated zone. In the Coastal Aquifer this flow rate has been shown to be $\sim$1 m/year (Gvirtzman and Magaritz, 1986). We show that an addition factor must be taken into account, i.e. the heterogeneous lithological properties of the aquifer and differences in water flow rates within the saturated zone. Over time, the continuous 'dripping' of high salinity water from the clayey part of the aquifer below the irrigated fields, where water flow is slower, should lead to deterioration in the quality of the underlying groundwater.

The results obtained in this study emphasis the importance of the WTR as a sensitive indicator for the amount and dynamics of anthropogenic pollution of phreatic aquifers. Most aquifers are monitored by testing the quality of pumping wells. We demonstrate that monitoring of the WTR is also an important component of the monitoring system and provides the capability to predict future non-point contamination.

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